UNIVERSIDAD POLITÉCNICA DE MADRID

**ESCUELA TÉCNICA SUPERIOR DE INGENIEROS DE
TELECOMUNICACIÓN**

**TCAD Modelling, simulation and characterization of
III-V multijunction solar cells**

TESIS DOCTORAL

Mario Ochoa Gómez

Ingeniero en Electrónica

Madrid 2018

UNIVERSIDAD POLITÉCNICA DE MADRID

Instituto de Energía Solar

Departamento de Electrónica Física

Escuela Técnica Superior de Ingenieros de Telecomunicación

**TCAD Modelling, simulation and characterization of
III-V multijunction solar cells**

TESIS DOCTORAL

AUTOR: Mario Ochoa Gómez
Ingeniero en Electrónica

DIRECTOR: Carlos Algora del Valle
Doctor en Ciencias Físicas

**Tribunal nombrado por el Magfco. Y Excmo. Sr. Rector de la
Universidad Politécnica de Madrid.**

PRESIDENTE:

VOCALES:

SECRETARIO:

SUPLENTE:

Realizado el acto de defensa y lectura de la Tesis en Madrid,
el día ____ de _____ de 2018.

Calificación:

EL PRESIDENTE

LOS VOCALES

EL SECRETARIO

A mis padres.

Resumen

La tecnología de células solares multiunión de materiales III-V ha sido capaz de desarrollar las células solares con las más altas eficiencias de conversión de radiación solar en electricidad. La alta eficiencia permite reducir considerablemente el tamaño y peso de los dispositivos, convirtiendo a este tipo de células en las preferidas para aplicaciones espaciales. Además, ofrecen un gran potencial para aplicaciones terrestres (concentración fotovoltaica) donde la reducción del tamaño permitiría disminuir su coste. A pesar de haber conseguido las más altas eficiencias, aún existe margen de mejora a nivel de dispositivo y sistema que deben ser abordados.

En consecuencia, esta tesis doctoral se centra en la simulación, caracterización y análisis de distintas células solares multiunión de materiales III-V tanto para aplicaciones terrestres como espaciales. El objetivo principal es desarrollar una herramienta TCAD de simulación de células solares multiunión (3, 4 o más uniones) basada en modelos de arrastre y difusión y en el uso de modelos cuánticos para tratar las uniones túnel. Gran parte de esta tesis está enfocada en la comparación de los resultados experimentales bajo diferentes condiciones de operación de las células con un único conjunto de parámetros de material y un conjunto dado de modelos físicos de semiconductores con el objetivo de validar los modelos. Además, se ha hecho especial énfasis en que los cálculos aquí mostrados estén basados en datos experimentales para proporcionar una visión cercana al estado del arte de las células solares multiunión y así mejorar su rendimiento.

En general, se ha llevado a cabo la simulación, caracterización y análisis individual de los componentes (subcélulas y uniones túnel) de una célula solar multiunión así como el estudio de las células solares multiunión integrando dichos componentes. Por ejemplo, se comienza con el estudio de cada una de las subcélulas que componen la célula solar de tres uniones GaIn-

P/Ga(In)As/Ge, así como las uniones túnel. En primer lugar, se analiza la célula de arseniuro de galio en donde la recombinación del perímetro juega un papel importante. Este fenómeno fue analizado con simulaciones 3D para distintos tamaños, geometrías y concentración de dopantes. Después, se ha implementado un modelo que describe el comportamiento de la célula solar de germanio con distintos tipos de emisor típicamente obtenidos por la formación de la unión pn en un reactor de crecimiento epitaxial (MOVPE). El modelo tiene en cuenta los perfiles reales de dopado en el emisor y ha sido utilizado para desglosar las pérdidas en dispositivos con distintos niveles de degradación asociados a la carga térmica durante el crecimiento. Para concluir el estudio de los componentes individuales de una célula multiunión, se ha llevado a cabo una validación del modelo de las uniones túnel y la célula de solar de GaInP bajo distintas condiciones de operación (en iluminación, oscuridad, etc.).

Una vez hecho esto, todos los componentes han sido integrados para formar la célula solar de tres y cuatro uniones: GaInP/Ga(In)As/Ge y GaInP/Ga(In)As/nitrato diluido/Ge. El modelo ha sido utilizado principalmente para analizar el comportamiento de dichas células así como para detectar donde se encuentran las mayores pérdidas de rendimiento. Se han analizado un par de ejemplos ("case studies") para la célula de tres uniones: 1) ¿cuáles son los factores que limitan (como la resistencia serie incluyendo heterouniones y uniones túnel) dichas células cuando operan a altas concentraciones luminosas (1000-5000 soles)? Además, se aportan algunas sugerencias de diseño para mejorar su rendimiento a estas elevadas concentraciones luminosas; 2) los efectos de la irradiación con un haz de protones de 10 MeV para estudiar la robustez de células de concentración en el ambiente espacial haciendo especial énfasis en la degradación de sus componentes individuales.

Se ha realizado también un análisis de células solares de nitratos diluidos que serían candidatos ideales para estructuras de cuatro uniones. Con el uso de la herramienta de simulación y datos experimentales, se han detectado las principales limitaciones y se han establecido los requisitos de dichas células para una exitosa integración en una célula solar de cuatro uniones. Además, se ha analizado la respuesta espectral de la subcélula de germanio debido a que puede convertirse en la célula que limita el rendimiento dentro de la estructura de cuatro uniones. También se ha optimizado la estructura de célula solar con el objeto de determinar las eficiencias prácticas que se podrían conseguir con las células de cuatro uniones que incorporan subcélulas de nitratos diluidos. Si se consiguen materiales de mayor calidad electrónica y se utilizan capas antireflectantes de amplio espectro (lo que ha sido demostrado recientemente), sería posible conseguir eficiencias cercanas al 47% operando en concentración y alrededor del 33% para aplicaciones espaciales.

Finalmente, también se ha estudiado teórica y experimentalmente la influencia de la temperatura en el acoplamiento luminiscente de distintas células solares multiunión (GaInP/GaAs y GaAs/GaInAs). El acoplamiento luminiscente fue evaluado en un rango amplio de temperaturas que cubren las típicas de operación de las células solares multiunión dentro de un concentrador (25-120°C).

Abstract

III-V multijunction solar cell technology has been able to develop devices with the highest conversion efficiencies of solar radiation into electricity. High efficiency solar cells are attractive because enables the size reduction of devices which directly translates into a reduction of the system components, thus the total cost. In fact, III-V multijunction solar cell technology is the preferred choice for solar panels in space applications and also they offer strong potential for terrestrial applications (concentrator photovoltaics or CPV). Although excellent devices have been already demonstrated, technical improvements at the system and solar cell level must still be attained to reach a further cost reduction.

Accordingly, this doctoral thesis covers the device simulation, characterization and analysis of different multijunction solar cells for space and high-concentration terrestrial applications. The ultimate goal is to build a tool for the simulation of multijunction solar cells (3, 4 and more junctions) based on the physical internal processes provided by drift-diffusion approximation together with the use of quantum models for tunnel junctions. Strong focus was made on the comparison to experimental results (under different conditions, namely dark, illuminated...) with the same single set of material parameters in order to provide a higher degree of confidence in our simulator. Furthermore, special attention was always paid to provide practical numbers based on current state-of-the-art devices.

Globally, the simulation, characterization and analysis of the individual components of a multijunction is carried out as well as the study of the whole multijunction solar cells by integrating their components (subcells and tunnel junctions). For instance, the analysis of each subcell of the GaInP/Ga(In)As/Ge 3J solar cell and the corresponding tunnel junctions is performed. First, the GaAs subcell is studied by taking into account perimeter recombination by

means of 3D simulations which exhaustively takes into account different geometries, sizes and doping concentrations at the base. A model for germanium solar cells with diffused profiles formed in a MOVPE environment was implemented which takes into account the real doping profiles of the emitter. The main limiting aspects were detected for several samples with different degrees of performance degradation. The tunnel junctions were properly calibrated to be used inside multijunction structures and the GaInP single junction solar cell was also analysed under different conditions (light, dark...).

Then, all these components were put together to form a 3J (GaInP/GaInAs/Ge) and 4J (GaInP/GaInAs/dilute nitride/Ge) multijunction solar cells in order to analyse them and dissect their main losses. A couple of case studies were carried out for the 3J structure: 1) the examination of the limiting factors (i.e., series resistance components including heterojunctions and tunnel junctions) for the operation under ultra-high irradiance (UHCPV) was carried out providing some basic suggestions for high efficiencies at concentrations from 1000-5000 suns and 2) the effects of a 10 MeV proton irradiation beam with different doses in order to study the radiation hardness of 3J concentrator solar cells for a 8-years mission in Low Earth Orbit (LEO). The latter was done by using component subcells as well as complete 3J structures in order to correlate the results and detect the radiation hardness of each component.

Dilute nitrides solar cells were also analysed through a multiple-data fitting process in order to determine their main limitations. The requirements of this subcell for the successful development of a 4J solar cell were determined. Then, some proposals are given to improve the germanium spectral response since it may become the limiting subcell in a 4J structure that would contain a high quality dilute nitride. Practical efficiencies around 47% for CPV applications and 33% for space applications are assessed by overcoming important constraints such as the achievement of a high material quality for the dilute nitride as well as the use of broadband anti-reflection coating.

Finally, the influence of temperature on the luminescent coupling of very high material quality multijunction solar cells (GaInP/GaAs and GaAs/GaInAs tandems) was also studied theoretically and experimentally. The luminescent coupling strength and linearity was evaluated in a wide range of temperatures covering the typical operating temperatures of multijunction cells inside a concentrator (25-120°C).

Contents

Contents	xix
List of figures	xxi
List of tables	xxxv
List of symbols	xxxix
List of acronyms	xlvi
1 Introduction	1
1.1 TCAD modelling and simulation	1
1.2 State of the art of TCAD modelling for multijunction purposes	3
1.3 Objectives	4
1.4 Thesis outline	6
1.5 Framework	7
2 TCAD simulation of multijunction solar cells: Fundamentals overview	9
2.1 Semiconductor equations	12
2.2 Carrier statistics	14
2.2.1 Effective density of states	14
2.3 Bandgap narrowing	15
2.4 Carrier generation-recombination models	16

2.4.1	Photogeneration	17
2.4.2	Radiative recombination	20
2.4.3	S-R-H recombination	20
2.4.4	Auger recombination	22
2.4.5	Surface recombination	22
2.5	Carrier mobility	23
2.6	Thermionic and thermionic field emission	25
2.7	Drift-Diffusion with position dependent band structure	26
2.8	Non-local band to band tunneling models	27
2.9	General boundary conditions	29
2.9.1	Ohmic contacts	29
2.9.2	Distributed specific contact resistance	30
2.9.3	Neumann boundaries	31
2.10	Conductors and insulators	31
2.11	Summary of models and general assumptions	32
2.12	Limitations	32
2.13	Particularities of the simulation framework	35
2.13.1	Dimensionality	35
2.13.2	Numerical precision	37
2.13.3	2D simulation assumptions for experimental data fitting	38
2.13.4	Data fitting procedure	41
2.13.5	Basic definitions for TCAD analysis	42
3	Simulation, characterization and analysis of GaAs, GaInP and Ge single junction solar cells and tunnel junctions	45
3.1	Introduction	46
3.2	Analysis of GaAs solar cells	46
3.2.1	Modelling perimeter recombination in a 3D TCAD environment	46
3.2.2	Model validation and analysis	66
3.3	Analysis of GaInP solar cells	70
3.3.1	Model validation and analysis	71
3.3.2	Design flexibility for multijunction solar cells by tuning the GaInP bandgap	73

3.4	Analysis of Ge subcells for advanced multijunction solar cells	75
3.4.1	Model customization for gradual emitters	76
3.4.2	Model validation	79
3.4.3	Impact of gradual emitter	81
3.4.4	Recovery of V_{oc} with light concentration	88
3.5	Tunnel junctions data fitting	89
3.6	Summary and conclusions	91
4	Simulation, characterization and analysis of GaInP/Ga(In)As/Ge 3J solar cells	93
4.1	Introduction	94
4.2	Modelling and characterization of GaInP:Sb/Ga(In)As/Ge 3J solar cells	94
4.2.1	Model validation and analysis	95
4.2.2	Layer-by-layer recombination losses under dark conditions	103
4.2.3	Layer-by-layer recombination losses under light conditions	107
4.3	Case study 1: Limiting factors of the semiconductor structure for Ultra-High Concentration (1000-5000 suns)	111
4.3.1	Methodology to assess the optimum design of multijunction solar cells for Ultra High Concentrator Photovoltaics (UHCPV)	113
4.3.2	Influence of top cell emitter	114
4.3.3	Influence of the top cell window	115
4.3.4	Recombination losses	118
4.3.5	Influence of heterojunctions	119
4.3.6	Voltage loss with light concentration due to perimeter recombination in 3J solar cells	122
4.3.7	Global optimization	123
4.3.8	Other multijunction solar cell architectures	125
4.4	Case study 2: Proton irradiation effects on concentrator lattice-matched GaIn- P/Ga(In)As/Ge triple junction solar cells for space applications	125
4.4.1	Experimental	127
4.4.2	Displacement damage dose analysis	128
4.4.3	Radiation damage on individual component cells	129
4.4.4	Radiation damage on triple-junction solar cells	134
4.5	Summary and conclusions	137

5	Four junction solar cell including a dilute nitride subcell for terrestrial and space applications	139
5.1	Introduction	140
5.2	Background	140
5.2.1	Dilute nitrides for solar cell applications	142
5.2.2	Annealing effects	144
5.2.3	State of the art multijunction solar cells including dilute nitrides	146
5.3	Modeling and characterization of GaNAsSb single junction solar cells	148
5.3.1	Device characterization	148
5.3.2	Model validation and analysis	151
5.3.3	Analysis of electric field-assisted collection	156
5.3.4	Minority carrier lifetime, mobility and carrier density	160
5.4	Modeling and characterization of 4J solar cell	163
5.4.1	4J solar cell manufacture	163
5.4.2	Preliminary device characterization	164
5.4.3	Model validation and analysis	167
5.4.4	Shunting behavior of GaNAsSb inside a 4J solar cell	170
5.4.5	Photocurrent requirements	172
5.4.6	Germanium subcell limitation and potential enhancements	175
5.4.7	Performance projections for space and terrestrial applications	179
5.5	Summary and conclusions	185
6	Influence of temperature on luminescent coupling in multijunction solar cells	187
6.1	Introduction	188
6.2	Background	188
6.2.1	Influence of temperature on MJSC performance	190
6.3	Experimental	191
6.3.1	Sample description	192
6.3.2	LC characterization procedure	193
6.4	Luminescent coupling characterization results	194
6.4.1	QE results	196
6.4.2	LC results	197
6.5	Luminescent coupling model and results	199

6.6	Subcell material quality evaluation in the presence of luminescent coupling . . .	202
6.6.1	Subcell analysis from dark IV models and internal voltages	202
6.6.2	Subcell internal radiative efficiency dependence on the injected current and temperature	206
6.7	Summary and conclusions	210
Future works		211
A Material parameters		213
A.1	Carrier lifetime, mobility and diffusion length	214
A.1.1	GaInP	215
A.1.2	GaAs	216
A.1.3	Ge	217
A.1.4	AlGaInP, AlInP and AlGaAs	220
A.2	GaNAsSb	221
A.2.1	Hall Mobility	222
A.2.2	Carrier lifetime and diffusion length	223
A.3	Band offsets	223
A.4	Refractive indices	224
A.5	Summary of material parameters and models	225
A.5.1	Mobility	225
A.5.2	BGN	226
A.5.3	Interface recombination	226
A.5.4	Tunnel junction parameters	226
A.5.5	General material parameters	227
Bibliography		231
Publications		269

List of Figures

1.1	Simulation hierarchy tool. Diagram adapted from [Dut00]. The dashed rectangle indicates more recent TCAD tools.	2
2.1	Device simulation sequence involving general stages on the design of semiconductor devices by using TCAD. Diagram adapted from [VG02]	10
2.2	Cross-section general scheme of a double junction solar cell structure (not to scale) showing the non-uniform background mesh and the region occupied by the secondary mesh required for tunnel models. ARC (violet), GaAs contact layer (green), top cell (blue), tunnel junction (gray), bottom cell (red) and electrodes (gold) are depicted. Boundary conditions indicated by arrows are extended along x-direction	11
2.3	Example of band profile of an abrupt heterojunction. Diagram adapted from [YEH93].	26
2.4	Energy band diagram schematic illustrating the TAT, NLTAT and NLBBT for a highly doped p-n junction.	28
2.5	Dimensionality of the solar cell structures used in this thesis. The 3D structure corresponds to a quarter of an entire solar cell with and square-inverted grid design.	36

2.6	V_{oc} loss due to dark areas in a 3J structure and estimated with three different approaches, namely: 2D-TCAD, quasi-3D circuit simulator and Eq. 2.63. Percentage numbers indicate the dark area with respect to the illuminated one. Symbols indicate calculated values and lines are a guide to the eye.	40
2.7	Flow chart we follow for the validation of material parameters and models. . .	42
3.1	Picture of the resulting square and circular GaAs diodes with different P/A ratios on a 2-inch wafer portion. Courtesy of P. Espinet-González.	51
3.2	Experimental dark I-V curves of square diodes for different (P/A) ratios of epi-wafer A.	51
3.3	Influence of surface trap densities N_t located at midgap on the dark I-V curve for P/A = 40.	53
3.4	Data fitting for: a) square devices and b) circular devices for #A epiwafer with P/A = 160, 53, 40 - in blue, red and green, respectively, and c) square devices for #B epiwafer with P/A = 160, 40 - in blue and green respectively. Lines are used for simulation and symbols for experimental data.	54
3.5	Dark a) $J_A - V$ curves and b) $J_p - V$ curves of square diodes for different (P/A) ratios of #A epiwafer.	55
3.6	Simulated 3-D plot of the electrostatic potential at equilibrium in P/A=160 diodes of the #A epiwafer. X coordinate shows a cross section of the diode where at 0 and 250 μm are placed at the borders of the structure where perimeter recombination appears. Y-direction (depth) at distances larger than 5 microns (substrate) is not shown for simplicity. The two dashed ellipses denotes the different potential barriers for carriers (see figure 3.7).	56
3.7	Zoom of the dashed ellipses of figure 3.6 representing the outline at perimeter ($V_{bis} = 0.16\text{V}$, green line) and bulk ($V_{bib} = 1.39\text{V}$, blue line) in the p-n junction. V_{bse} (0.6V) denotes the potential barrier seen by a carrier from the emitter bulk to the emitter surface (away from the depletion region where the potential is flat at bulk) if it moves in the same x coordinate. V_{bsb} (0.56V) is for case in the base region.	57

3.8	3-D plot of the potential at the p-n junction near the surface perimeter ($x=0$ μm) for #A (left) and #B (right) epiwafers under forward bias: a) 0.7V, b) 1V and c) 1.3V. The depth and width (along x coordinate) of the structure sides is shortened for simplicity. At the ground of the figures letter <i>E</i> denotes emitter while <i>B</i> is for base region.	58
3.9	Semi-logarithmic 3-D plot of recombination rate at the p-n junction for #A (left) and #B (right) epiwafers under forward bias: a) 0.7V, b) 1V and c) 1.3V. The depth and width (x coordinate) of the structure sides is shortened for simplicity.	60
3.10	Experimental measurements of the dark I-V curve for two representative diodes ($P/A=160$) manufactured on #A and #B epiwafers showing the influence of the base doping level. The blue line corresponds to the current ratio of both diodes as a function of the bias.	61
3.11	Simulation of the recombination rate contribution for radiative and non-radiative processes for a $P/A=160$ diode: a) #A epiwafer and b) #B epiwafer. Auger recombination is negligible with respect to the other recombination mechanisms so, for the sake of simplicity it is omitted.	62
3.12	Simulated dark I-V curve of a GaAs solar cell with a size of 0.01 cm^2 ($P/A=40$) varying the p-base doping level.	63
3.13	Simulation of the contribution of bulk and perimeter currents for a solar cell with a size of 0.01 cm^2 ($P/A=40$) manufactured on epiwafer #A.	63
3.14	Simulated dark current density ratio between square and circular devices as a function of their P/A for two bias voltages. Lines are a guide to the eye.	65
3.15	Experimental and simulated dark I-V curve of the GaAs solar cell together with the contribution from radiative and non-radiative recombinations.	67
3.16	Experimental internal and external quantum efficiency together with the calculated contribution of different regions of GaAs solar cell with standard design. Bottom: Reflectance of the same solar cell structure. Symbols are used for experimental data while lines for simulations. The calculated depletion layer width is 230 nm. Carrier collection efficiency for each layer is shown within brackets.	68
3.17	EQE contribution of the window layer for three different cases: 1) current devices (green), 2) assuming no surface recombination (red) and 3) assuming complete or ideal collection (blue). Solid lines correspond to GaInP window layer while dashed lines correspond to an AlInP window layer.	68

3.18	Experimental and simulated I-V standard GaAs solar cell parameters as a function of light concentration.	70
3.19	Current density of a quarter of a 1mm ² GaAs solar cell at 1V for 1 sun (a) and 700 suns (b).	70
3.20	Experimental and simulated dark I-V curve of the GaInP solar cell whose structure is shown in Table 3.7 together with the contributions from radiative and non-radiative recombination.	72
3.21	Experimental internal and external quantum efficiency and the calculated contribution for the GaInP solar cell. Bottom: Reflectance of the same solar cell structure. Symbols are used for experimental data while lines for simulations. The BSF contribution is not zero mainly because the total thickness of the solar cell does not absorb 100% of light. Depletion layer width is 336 nm. Carrier collection efficiency for each layer is shown within brackets.	73
3.22	(a) Calculated short circuit current density and (b) open-circuit voltage of the GaInP subcell latticed-matched to Ge as a function of the bandgap energy and the thickness of the base layer under AM1.5d ASTM G173-03.	75
3.23	Top: Schematic of the baseline structure (not scaled to real dimensions) and model assumptions for the Ge emitter. Bottom: Non-uniform doping profiles at the Ge emitter used in the simulations (from ECV measurements) for the three samples analysed. The curves are shown from the beginning of the emitter until the junction depth is reached (i.e. $N_D=BCC$). Vertical dashed lines indicate the intersection of emitter #1 and #2 for each solar cell. X_E corresponds to the total emitter thickness, including E1 and E2.	78
3.24	Experimental (black square filled symbols) and simulated (red solid lines) IQE (top), EQE (middle) and reflectance (bottom) curves for the three samples analysed in this section (i.e. #A2, #A3, #E3). The contributions of each region in the structure is also depicted for each IQE curve (dashed lines). The CE calculation (for $\lambda > 885\text{nm}$) is shown within brackets for the AM1.5d ASTM-G173 solar spectrum.	80
3.25	Experimental and calculated dark I-V curves for the three samples.	80
3.26	(a) Conduction band energy at equilibrium for different experimental emitter doping profiles. (b) Valence band energy at equilibrium for different experimental emitter doping profiles.	82

3.27	Simulated J_{sc} (a and c) and V_{oc} (b and d) as a function of the effective S_E and $L_{h,E}$ of structures #A2 (a and b) and #E3 (c and d) with their corresponding emitter characteristics (i.e., gradual emitter and thicknesses). Dashed thick lines indicate the range of values that fit experimental V_{oc} and J_{sc} independently, while the yellow stars stand for the overlapping of the dashed thick lines corresponding to the best data fitting.	84
3.28	Integrated recombination rate values at 160mV for <i>etched</i> solar cell #E3 with two different hole mobilities at E1. Layer notation is that of Fig. 3.23.	88
3.29	Simulated (lines) and experimental (symbols) V_{oc} as a function of light concentration for the two as-grown samples (#A2 and #A3) and the etched one (#E3).	89
3.30	Experimental and simulated I-V for the AlGaAs/GaAs (left) and AlGaAs/-GaInP tunnel junction by using non-local tunnel junction models and trap-assisted tunnelling models.	90
3.31	Experimental and simulated EQE of Ga(In)As subcells (with and without ARC) with two different tunnel junctions. A GaInP layer of 750 nm acts as an optical filter [Bar+14].	91
4.1	(a) Nominal structural design of the GaInP/Ga(In)As/Ge triple junction analysed. (b) Band diagram in equilibrium conditions for the 3J solar cell. A MgF ₂ /ZnS anti-reflection coating of was deposited in some devices.	96
4.2	Experimental (symbols) and simulated (lines) external quantum efficiency (EQE), internal quantum efficiency (IQE) and R for the GaInP/Ga(In)as/Ge 3J solar cell. Dashed lines indicate the quantum efficiency (QE) contribution of each layer within the corresponding subcell. The numbers within brackets correspond to the J_{sc} of simulated curves while the numbers without brackets correspond to the experimental ones, both calculated using the AM1.5d ASTM-G173 spectrum.	99
4.3	Dark and light J-V curves for the 3J solar cell and its corresponding subcells.	101
4.4	Solar cell parameters of calibrated concentration measurements of a GaInP/Ga(In)As/Ge triple junction solar cell. The baseline structure has a measured peak efficiency of 39.2% at 400 suns and about 37% at 1000 suns	103

- 4.5 Top graph: recombination current density at different regions for: Ga(In)As (left) and Ge (right) as a function of voltage bias. Black dashed horizontal line indicates the current value matching the J_{sc} of this multijunction solar cell at 1-sun. Middle graph: recombination by types (radiative and non radiative) for the dominant layers, namely emitter+ IR_{WE} (E) and base (B). Bottom graph: fraction of total recombination occurred at base (red) and emitter+ IR_{WE} (green) as a function of voltage bias. 104
- 4.6 Experimental (symbols) and simulated (lines) dark J-V curves of GaInP:Sb sub-cell for different values of minority carrier lifetimes: base (left) and emitter (right). 105
- 4.7 Top graph: recombination current density at different regions of GaInP:Sb as a function of voltage bias for three different cases: *best emitter* (a), *best fit* (b) and *best base* (c). Black dashed horizontal line indicates the current value that match the J_{sc} of this multijunction solar cell at 1-sun. Middle graph: radiative and non radiative recombination for the dominant layers, namely emitter+ IR_{WE} (E) and base (B). Bottom graph: fraction of total recombination occurred at base and emitter+ IR_{WE} as a function of voltage bias. 108
- 4.8 Fraction of recombination under dark (solid) and illuminated (dashed) conditions by regions of each subcell: GaInP:Sb (left), Ga(In)As (middle) and Ge (right). 109
- 4.9 Recombination rate and hole concentration at ~ 1 -sun as a function of the depth within the GaInP:Sb subcell (left), Ga(In)As (middle) and Ge (right). The cross section is taken at 1/3 of the total length (illuminated area) of Fig. 4.1. 110
- 4.10 Solar cell parameters of calibrated concentration measurements of a GaInP/Ga(In)As/Ge triple junction solar cell. The baseline structure has a measured peak efficiency of 39.2% at 400 suns and about 37% at 1000 suns. 115
- 4.11 Contour plot of efficiency as a function of the top cell doping density and concentration. The top cell emitter doping is $5 \cdot 10^{18} \text{ cm}^{-3}$ and the thickness is 175 nm. 116
- 4.12 Cross-sectional color map of current density at maximum power point ($\sim 3 \text{ V}$) and 5000 suns of top layers in the GaInP subcell for two window doping densities (a) 10^{18} cm^{-3} and (b) 10^{19} cm^{-3} 117

- 4.13 Fraction of different recombination losses within the multijunction solar cells (cross-section view) at 5000 suns. The recombination losses are calculated at open circuit. Please note that in order to show this plot clearly, the depth in the structure is not scaled and does not correspond to the real thickness of the layers. 119
- 4.14 Solar cell parameters at 5000 suns as a function of doping density of the top cell back surface field (BSF) layer for a high VBO $\sim 700\text{meV}$ (red lines) and for a nominal VBO $\sim 480\text{meV}$ (black dashed lines). 121
- 4.15 Valence band energy at equilibrium between AlGaInP/AlGaAs (top cell back-surface field (BSF) and tunnel junction anode). The effective barrier height for each case is: 220 (black dashed line), 430 (red line) and 480 meV (green dashed line). Different transport processes are illustrated such as tunnelling and thermionic emission corresponding to the main mechanisms to overcome the potential barrier formed at the heterointerface. 122
- 4.16 Absolute and relative —with respect to $3J - V_{oc}$ losses due to perimeter recombination as a function of light concentration. The device P/A ratio is 40. Ga(In)As base doping level is $2 \cdot 10^{17} \text{ cm}^{-3}$ 123
- 4.17 Efficiency as a function of light concentration of a 1 mm^2 GaInP/Ga(In)As/Ge triple junction solar cell with an inverted-square metallization grid for different metal sheet resistances. The optimized structure has a top cell window doping level of 10^{20} cm^{-3} and 25 nm thickness, the 50 nm-thick top cell emitter doping level is 10^{19} cm^{-3} doped. 124
- 4.18 Degradation in a) J_{sc} , b) V_{oc} , c) FF and d) P_{max} of Ge, GaAs and GaInP/Ge solar cells for in situ measurements at different D_d of 10 MeV proton irradiation. Two different devices are shown for each solar cell type. An experimental uncertainty of 2% can be expected. Solid lines correspond to the data fitting of Eq. 4.1. 130
- 4.19 Dark I-V curves for beginning of life (BOL) and EOL for GaInP/Ge, GaAs and Ge solar cells. 131
- 4.20 External Quantum Efficiency measurements and corresponding data fitting of the GaAs solar cell before (BOL) and after (EOL) 10 MeV proton irradiation. (b) Calculated photogeneration rate (photogeneration rate (PGR)) of the GaAs solar cell structure. BSF PGR is augmented by a factor of 10^6 . No antireflection coating (ARC) has been deposited 132

4.21	Dark I-V curves of representative GaAs solar cells at BOL and end of life (EOL) and their corresponding data fitting. Black lines show the slopes of typical ideality factors of the two diode model.	133
4.22	Normalized a) J_{sc} , b) V_{oc} , c) FF and d) maximum power output of two lattice-matched triple-junction GaInP/GaAs/Ge solar cells as a function of the D_d . The corresponding data fitting to Eq. 4.1 is shown in solid red lines while the fitting parameters are shown in the inset table.	135
4.23	External Quantum Efficiency at BOL and EOL of each subcell of a representative lattice matched triple-junction solar cell GaInP/GaAs/Ge. Dashed blue line shows the EQE of the Ge-subcell after correction. Black and red dashed lines correspond to the EQE measured in the single junction GaAs solar cell. No ARC has been deposited onto the solar cell.	136
4.24	Light I-V curve measured under 1-sun AM0 spectrum of a representative triple junction solar cell at BOL and EOL and their corresponding solar cell parameters. No ARC has been deposited onto the solar cell.	137
5.1	Band gap energy versus lattice constant for germanium and different III-V (N) alloys. The orange fringe shows the range of desired bandgap for multijunction solar cells with 4 or more junctions on Ge (up to 6) [Jon+13]. Blue lines correspond to the bandgap of dilute nitrides calculated by using the band anti-crossing (BAC) model and parameters taken from [VM03]. Vertical green line is placed at the germanium lattice constant.	142
5.2	Schematic structure of GaNAsSb single junction solar cell. The buffer layer also acts as a BSF layer.	149
5.3	QE characterization of champion solar cells. Five or more solar cells have been measured showing similar results within typical deviations associated to sample-to-sample variation.	149
5.4	EQE and reflectance for the 4 epiwafers studied in this chapter. The contribution of the different semiconductor layers to the total EQE curve is also depicted (dashed lines). Symbols correspond to experimental curves (circles for EQE and crosses for reflectance). Solid lines correspond to data fitting by modifying the average doping concentration at the absorber (and lifetime) while dotted lines correspond to the fits obtained by modifying only the minority carrier lifetime of the absorber.	152

- 5.5 Left: Experimental (crosses) and simulated (circles and triangles) V_{oc} for all devices with different N_A and $\tau_{e,abs}$. Right: Difference between quasi-Fermi energies for electrons and holes at the p-n junction for device N2976 at different doping concentrations and electron lifetimes at the absorber. Two different set of parameters of N_A and $\tau_{e,abs}$ that achieved successful QE data fitting are shown. Fixed N_A corresponds to the nominal or UID expected ($5 \cdot 10^{17}$ for N2980 and $5 \cdot 10^{15} \text{ cm}^{-3}$ for the rest.). The electron lifetime fixed corresponds to fit 1 case (70 ps). 154
- 5.6 Experimental light I-V curves using a 940-nm LED – which is only absorbed in the GaNAsSb region – with intensities close to 1 sun (circles) and 2 suns (diamonds). No ARC has been deposited onto the solar cells. 157
- 5.7 Left: Contour plot of the EQE values at a 1000 nm wavelength as a function of N_A and W_b . Right: Electric field profile across the p-n junction as a function of N_A for solar cells with $W_b=2\mu\text{m}$. The electric field spans to a depth of $1.2 \mu\text{m}$ for clarity. 158
- 5.8 Left: Carrier collection with zero reflection losses versus thickness of an ideal GaNAsSb absorber (solid line) and calculated values (symbols) of our real solar cells for different bias voltages, i.e. from -8V (blue) to 0.35V (green). Right: Electric field profile across the p-n junction for different bias voltages illuminated with a beam of $1 \mu\text{m}$ wavelength light for two different doping concentrations: $5 \cdot 10^{15}$ (solid) and 10^{14} cm^{-3} (dashed). The thickness of the absorber is $3\mu\text{m}$. Carrier collection is evaluated in the useful wavelength range in a 4J solar cell (885-1200nm) for both ideal and real devices operating at different bias voltages. Each symbol's color of left figure corresponds to the ones of the electric field profile of right figure. 159
- 5.9 Set of contour plots representing the I-V parameters at 1-sun AM1.5d ASTM-G173 solar spectrum for GaNAsSb solar cells as a function of both minority carrier mobility and lifetime for different doping concentrations assuming a $3 \mu\text{m}$ -thick p-type absorber. Both LGA and LGB stand for linear gradual doping (different ranges) from bottom to top of the absorber. 163
- 5.10 Schematics of the semiconductor layer structure corresponding to the 4J solar cell analysed in this chapter. The Metalorganic Vapour Phase Epitaxy (MOVPE) growth was carried out at IES-UPM facilities while the MBE growth took place at NTU. 165

- 5.11 Experimental EQE of a representative 4J solar cell ($1\mu m$ GaNAsSb absorber) manufactured (solid lines) and the control cells (dashed lines). The control cells are both GaInP/Ga(In)As/Ge 3J cell and a GaNAsSb 1J solar cell. For a proper comparison, the wavelength range used for J_{sc} calculation has been restricted to $\lambda > 885$ nm for the GaNAsSb solar cell and $\lambda > 1200$ nm for the Ge cell and their corresponding EQE's have been cutted for better visualization. For instance, the J_{sc} of the Ge subcell considering the whole range from 885 nm is 10.35 mA/cm^2 166
- 5.12 Spectral EL for different injection currents showing different light emission and EL peaks coming from GaInP (1.83 eV), Ga(In)As (1.4 eV) and Ge (0.7 eV) subcells. No GaNAsSb light emission has been detected at room temperature. . 166
- 5.13 Measured (symbols) and calculated (lines) IQE (top), EQE (middle) and reflectance (bottom) for the 4J solar cell manufactured by the hybrid MOVPE+MBE technologies. 167
- 5.14 Left – Experimental (symbols) and simulated (lines) light I-V curves of the 4J solar cell under 1-sun both ASTM G173 and AM0 spectra. An inset table shows the experimental and simulated (inside parenthesis) I-V parameters. Right – Experimental and simulated dark I-V curve of the same solar cell. 169
- 5.15 Left – Simulated subcells and complete 4J cell I-V curves under 500-suns AM1.5d ASTM G173 spectrum. Right – Magnification of the region close to short-circuit conditions to highlight the increase in the 4J J_{sc} by summing up the behavior of all the subcell I-V curves. 171
- 5.16 Energy band diagram at (a) equilibrium, (b) J_{sc} , (c) P_{max} and (d) V_{oc} . Each color corresponds to different regions within the structure of Fig. 5.10. Gray regions contain each tunnel junction with barrier layers (if used) and buffer layers. Note the difference in the vertical axes of these graphs. 172
- 5.17 J_{sc} of the 4J solar cell by considering measured QE's for GaInP, Ga(In)As and Ge for different dilute nitride QE magnitudes as a function of its bandgap. The cases where Ge is ideal or real (black lines) are also depicted. The calculations have been made at 300K for J_{sc} targets of (a) 14 mA/cm^2 and (b) 13.5 mA/cm^2 . 175

- 5.18 IQE and absorption calculated using the term $[1 - \exp(-\alpha L)]$, being L the thickness of the germanium slab considered (values in μm) assuming absorption=collection. No free-carrier absorption (FCA) was considered and $R_{back} = 0$. Red symbols show a typical state-of-the-art IQE of germanium solar cell with thickness of $150 \mu\text{m}$ and doped $N_A = 10^{18} \text{cm}^{-3}$ 176
- 5.19 Ge subcell I-V parameters as a function of base thickness for different solar cell with and without BSF at 1-sun for both spectra: AM0 and AM1.5d. Values in the legends (0,100,1000 in cm/s) correspond to the back surface recombination velocity assumed (S_b). Note the different y-scale for J_{sc} and efficiency for both spectra. No FCA either ARC was considered and $R_b = 0$. The structure without BSF has a diffusion length $\sim 70 \mu\text{m}$ 178
- 5.20 Simulated EQE of each subcell of the GaInP/Ga(In)As/GaNAsSb/Ge 4J solar cell. The EQE's of the GaNAsSb subcell is depicted for four different factors of the current diffusion length (1, 2, 5 and 10). The lower response in the GaAs subcell is due to its thickness thinner ($1.25 \mu\text{m}$) than usual. A bilayer ARC of $\text{MgF}_2(110\text{nm})/\text{ZnS}(70\text{nm})$ has been assumed and the corresponding reflectivity of the 4J solar cell is shown as a black solid line 181
- 5.21 Simulated external quantum efficiency (black dashed lines) of the 4J subcells. The corresponding reflectance is shown by a solid gray line. The region where photons are lost by recombination is shown in blue while the region corresponding to reflection loss is shown in red. Each junction has enough thickness to absorb above 98% average of the incoming light in their corresponding wavelength range. In the legend, a summary of collected and lost photocurrent is depicted. 182
- 5.22 Simulated External Quantum Efficiency and reflectivity of the GaInP/GaAs/Ga(In)NAs(Sb)/Ge 4-J solar cell analysed in this thesis. The structure assumes a conventional $\text{MgF}_2(110\text{nm})/\text{ZnS}(60\text{nm})$ ARC (gray line). The improved ARC taken from [Per+14] is represented by a black dashed line 184
- 5.23 Performance as a function of concentration of the optimised 4J solar cell under AM1.5d ASTM-G173. 185
- 6.1 Schematic for a dual junction solar cell showing the photon emission from radiative recombination and the re-absorption of such photons in the same subcell (PR) or the the lower bandgap subcell (LC). 189

6.2	Design of the two structures analysed. The solar cell active areas are 0.25 and 0.1cm ² for ML732 and MM708, respectively. Horizontal axis indicated the lattice constant.	192
6.3	Schematic of 1-sun adjustable simulator with Xenon lamp and various LEDs light sources. An example of the spectrum measured by the spectroradiometer is also depicted at the left part of the figure. The LEDs shown correspond to the configuration used in the luminescent coupling (LC) characterization	194
6.4	EQE of a GaInP/GaAs dual-junction solar cell for different 470-nm LED intensities without any LC correction procedure applied.	196
6.5	(a) EQE measurements (top) of the GaInP/GaAs two-junction cell and (b) the GaAs/GaInAs at different temperatures once corrected by luminescent coupling following the procedure described in [Ste+13c]. Reflectance of each solar cells is depicted at bottom figures of (a) and (b) at different temperatures	197
6.6	J_{SC} of GaInP/GaAs (a) and GaAs/GaInAs solar cell (b) at different temperatures for measurements (top) with background light X_2 , and (bottom) without the background light when X_1 is varied. Markers are data and lines are fits. . .	198
6.7	Luminescent coupling parameters: (a) η_{12} and (b) ϕ_1 fitted from the measurements for the GaInP/GaAs cell, ML732 (blue region filled circles) and the GaAs/GaInAs cell, MM708 (red region and filled squares).	201
6.8	J_{01} and J_{02} for GaInP in the ML732 device. C_1 and C_2 (in units of mA/cm ²) correspond to the proportionality constants of Eqs. 6.4 and 6.5, respectively . .	204
6.9	J_{01} and J_{02} for GaAs in the MM708 device. C_1 and C_2 (in units of mA/cm ²) correspond to the proportionality constants of Eqs. 6.4 and 6.5, respectively . .	204
6.10	Temperature dependence of W_{oc} and $V_{oc} - V_p$ for each top cell in the two structures analysed.	205
6.11	Contour plot of $\eta_{int}(J, T)$ of the top cells: (a) GaInP in ML732 (b) and GaAs in MM708	207
6.12	Internal radiative efficiencies at one sun-equivalent injected current calculated by optical modelling described in [Ste+13a]. Dashed lines are the corresponding fitting curves calculated with Eq. 6.10	208

- A.1 Minority carrier lifetime found in literature (symbols) for p-type samples (no data found for n-type). Haegel data (low level injection conditions) shows annealed and as-grown MBE-samples (A, AG, respectively) [Hae+14]. Dagan et al. [Dag+16] and Perl et al. [Per+17] (low level injection conditions) are MOVPE-samples. Schultes et al. data is for MBE-samples and doping values between $10^{15} - 10^{16} \text{ cm}^{-3}$ are estimated (unintentionally doped (UID) samples). The high values from Dagan et al. suggest that measurements were performed possibly in high injection conditions. Since our GaInP solar cells are clearly dominated by SRH, the effective lifetime would be very similar to that of SRH one. 215
- A.2 Majority and minority carrier mobilities found in literature (symbols) and the ones calculated by using Sotoodeh equations (lines) [Sot+00]. Haegel et al. is for MBE-grown GaInP [Hae+14] measured in two different crystallographic orientations. Jakomin et al. data is taken from [Jak+12]. 215
- A.3 Minority carrier lifetime (SRH) found in literature (symbols). Figure adapted from Lumb et al. [Lum+14] (see references therein for experimental data). Lines calculated by using Eqs. and fitting parameters also from Lumb et al. [Lum+14]. 216
- A.4 Electron (left) and hole (right) mobilities for n-type and p-type GaAs. Niemeyer, Tiwari, Lundstrom, Sotoodeh and Lovejoy data are taken from [Nie+17], [TW90], [Lun+90], [Sot+00] and [Lov+92], respectively. Input model lines were calculated by following the equations from [AD97]. 217
- A.5 Carrier lifetime found in literature for n-type (filled symbols) and p-type Ge (empty symbols). See Gaubas et al. and references therein [Gau+07] for the parameters used in these calculations (Eq. A.1). Lines show the calculated values by solving the analytical equations taken from [GV06] for different excitation levels. Dashed lines correspond to the values with $k \geq 1$. This figure is adapted from [GV06] and updated including Yoon et al. data for commercially available Ge material for solar cells [Yoo+05]. 218
- A.6 Calculated minority carrier mobility for n-type and p-type germanium and experimental data taken from [Yoo+05]. $\gamma = 0.55$ and $\gamma = 0.58$, $\mu_l = 1900$ and $\mu_l = 3900$ and $N_{ref} = 7 \cdot 10^{16} \text{ cm}^{-3}$ and $N_{ref} = 10^{17} \text{ cm}^{-3}$ for n-type and p-type, respectively. 218

A.7	Minority carrier diffusion length as a function of doping concentration considering the effective carrier lifetime (Auger, SRH and radiative components).	219
A.8	Majority electron mobility in AlInP lattice matched to GaAs taken from [Gud+08; KF97] (empty symbols) and [Dai+15] (which corresponds to MBE-grown samples, filled symbols). Solid line corresponds to the values calculated from Equation A.3.	221
A.9	Minority carrier lifetime measured by TRPL in DH for p-type and n-type GaNAsSb (1 eV) samples and assuming nominal — or typical for UID samples— doping concentrations. Doping and τ_{SRH} values deduced from GaNAsSb single junction solar cell structures by multiple data-fitting (QE and V_{oc} , see section 5.3.2) are also depicted (triangles).	223
A.10	Real part of refractive index for several III-V materials as well as GaNAsSb and germanium. GaInP(o) stands for partially-ordered GaInP while GaInP(d) stands for disordered GaInP.	225
A.11	Extinction coefficient for several III-V materials as well as GaNAsSb and germanium. GaInP(o) stands for partially-ordered GaInP while GaInP(d) stands for disordered GaInP.	225

List of Tables

2.1	Summary of some of the typical methods for photo generation calculation in solar cells. BPM stands for beam propagation method, RCWA for rigorous coupled-wave analysis and FDTD for finite difference time domain analysis. . .	19
2.2	Main features of different dimensions for multijunction solar cell simulation (based on a 4J solar cell). ARC stands for anti-reflection coating.	37
3.1	Structure of n/p GaAs diodes for the two #A and #B epiwafers.	50
3.2	Geometrical characteristics of the square and circular diodes manufactured. . .	50
3.3	Trap parameters at surface and in bulk used in simulations of diodes manufactured on #A and #B epiwafers.	55
3.4	Voltage values where bulk current (I_b) is equal and five times greater than perimeter current (I_p) for different solar cell sizes.	64
3.5	Semiconductor layer structure of the GaAs solar cell.	66
3.6	I-V parameters for experimental and simulated GaAs solar cells at one sun under the AM1.5d ASTM-G173 direct spectrum. The I-V parameters under certain assumptions avoiding specific losses (SRH) are also shown. The minority carrier lifetimes assumed infinite correspond to simulations neglecting the non-radiative recombination (SRH). V_{oc} values would increase about 10 mV by considering ARC deposition.	69
3.7	Semiconductor layer structure of the GaInP solar cell.	71

3.8	I-V parameters for experimental and simulated GaInP solar cells at one sun under the AM1.5d ASTM-G173 direct spectrum. The I-V parameters calculated under certain assumptions avoiding specific losses (SRH) are also shown. The minority carrier lifetime assumed infinite corresponds to simulations neglecting the non-radiative recombination (SRH). V_{oc} values would increase about 10 mV by considering ARC deposition.	73
3.9	Measured and simulated J_{sc} , V_{oc} and FF of representative devices of structures #A2, #A3 and #E3. Experimental values correspond to the champion cells. Relative standard deviations for all measured devices (about 5-10 for each solar cell) were lower than 2% for J_{sc} and FF and within the range of 0.3-0.9% for V_{oc}	81
3.10	Fraction of recombination losses for different scenarios at the interface window/emitter (W/E), emitter (E) and base (B) under dark conditions (close to virtual open circuit voltage) for samples analysed in this section (#A2, #A3 and #E3). The range of values extracted from the sensitivity analysis for $\mu_{h,E}$, $\tau_{h,E}$ and S_E is shown. The scenarios involve cases for maximum and minimum threshold values of $\mu_{h,E}$ and considering infinite or absence of interface recombination between window and emitter. The range of values extracted was established by assuming that the multiple data fitting for J_{sc} (keeping similar IQE shape) and V_{oc} did not deviate more than 2% and ± 2 mV, respectively. The diffusion length for electrons at the base (L_b) is also depicted. The emitter and base losses were obtained by integrating the recombination rate over each region including the space charge region in each zone.	86
4.1	QE contribution and collection efficiency for the main active regions of each subcell of the 3J solar cell. The contribution from the rest of the layers is negligible and is not shown for simplicity.	100
4.2	Experimental and simulated I-V parameters for the 3J solar cell and their corresponding subcells illuminated at 1-sun AM1.5d ASTM-G173 spectrum. The V_{oc} gain by neglecting Sockley-Read-Hall (SRH) recombination losses is also depicted.	102

4.3	Band discontinuities for different heterojunctions formed at the MJSC of Figure 4.1 taken from the literature. All band discontinuities are calculated applying Anderson's rule. The band discontinuity calculation starts from experimental measurements of the valence band offset or using nominal electron affinities. When electron affinities are used, the resulting band discontinuities are comparable with literature. In the case of the $(\text{Al}_{0.2}\text{Ga}_{0.8})_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ band offset, it is calculated by applying Anderson's rule [Sil16] but using the nominal electron affinities taken from [Gud+09a; LRS96], respectively. Bold and italic numbers correspond to barriers for majority carriers, electrons (ΔE_{cv}) or holes (ΔE_{vb}). Heterojunctions found in tunnel junctions are not included in this table because non-local tunnelling models (expected dominant transport process) are used to simulate carrier transport instead of thermionic and thermionic-field emission boundary conditions.	120
4.4	Solar cell structures subjected to 10MeV proton irradiation. The GaAs solar cells were grown on a highly doped p-type GaAs substrate while the other solar cells were grown on Ge substrates. Two different devices have been irradiated for each solar cell type and their corresponding fluences are shown in the last two columns	128
4.5	Fitting parameters of Eq. 4.1 to J_{sc} , V_{oc} and P_{max} degradation curves of Fig. 4.18.	130
4.6	Absolute differences and relative loss in I-V parameters between BOL and EOL conditions for the solar cells analysed under 1-sun AM0 spectrum. Negative values do not indicate a gain in performance, but values within the measurement uncertainty.	137
5.1	Summary of the general requirements and challenges for subcell materials (GaInNAs, GaNAsSb and GaInAsNSb) for 4 or more junctions solar cells on Ge (up to 6)	145
5.2	Average I-V parameters of the GaNAsSb single junction solar cells. *The epi-wafer N2980 has a nominal absorber doping $N_A=5\cdot 10^{17}\text{ cm}^{-3}$. The standard deviation is shown between parenthesis. Five or more solar cells were measured for each epiwafer.	150
5.3	Fitting parameters of the absorber region for two different fittings in all epiwafers.	155
5.4	Nominal and modified (in red) thicknesses employed for reflectance data fitting.	156

5.5	Summary of the J_{sc} calculated from the experimental and simulated QE curves for each subcell and by using the AM1.5d ASTM-G173 spectrum.	168
5.6	Available J_{sc} for each subcell of the 4J structure for space and terrestrial spectra. The calculated J_{sc} from simulated IQE curves (see Fig. 5.21) are also shown for both spectra. A thick absorber (3 μ m) has been assumed exhibiting a 98% of light absorption for all subcells.	182
6.1	Fitting parameters of Eq. 6.10	209
A.1	Summary of characterization techniques used in this thesis to obtain the main material parameters of GaNAsSb as well as the theoretical method of extraction.	222
A.2	Carrier concentrations measured by ECV and majority carrier mobilities measured by Hall for a set of GaNAsSb samples with different nominal doping concentrations and dopant types.	222
A.3	Tunneling parameters for non local band to band tunnel models and trap-assisted tunneling	226
A.4	Summary of semiconductor material parameters used for simulations of the main layers of GaInP solar cells.	227
A.5	Summary of semiconductor material parameters used for simulations of the main layers of GaAs solar cells.	228
A.6	Summary of semiconductor material parameters used for simulations of the main layers of Ge and GaNAsSb solar cells.	229

List of symbols

A_{illum}	Illuminated solar cell area
A_{total}	Total solar cell area
B	Radiative recombination coefficient
c	Speed of light speed
C_n	Auger coefficient for electrons
C_p	Auger coefficient for holes
D_d	Displacement damage dose
D_L	Debye Length
D_n	Diffusion coefficient of electrons
D_p	Diffusion coefficient of holes
η_i	Coupling efficiency from junction i
η_{ext}	External radiative efficiency
η_{int}	Internal radiative efficiency
δ	Tunneling factor
E_C	Conduction band energy
E_F	Fermi level

E_g	Energy bandgap
E_i	Intrinsic Fermi level
E_{ph}	Photon energy
E_t	Trap energy level
E_V	Valence band energy
ϵ	Permittivity
ε	Energy
$\mathcal{F}_{1/2}$	Fermi-Dirac integral
FF	Fill Factor
g	Degeneracy factor
G	Generation rate
G_n	Generation rate for electrons
G_p	Generation rate for holes
h	Planck Constant
J_{01}	Saturation current density in the quasi-neutral region
J_{02}	Saturation current density in the depletion region
J_{ext}	Externally induced photocurrent density
J^{LC}	Luminescent coupling current density
J_n	Electron current density
J_p	Hole current density
J_{peak}	Peak tunneling current density
J_{per}	Perimeter current density
J_{ph}	Photogenerated current density

J_{rec}	Recombination current density
J_{sc}	Short circuit current density
k	Boltzmann constant
L_D	Diffusion length of carriers
L_e	Diffusion length of electrons
$L_{h,E}$	Diffusion length of holes at the emitter
$L_{e,B}$	Diffusion length of electrons at the base
L_p	Diffusion length of holes
L_s	Surface diffusion length
m	Number of junctions
m_e^*	Effective mass for electrons
m_h^*	Effective mass for holes
$\mu_{e,B}$	Electron mobility at the base
μ_n	Electron mobility
μ_p	Hole mobility
$\mu_{h,E}$	Hole mobility at the emitter
n	Electron concentration or ideality factor
n_i	Intrinsic carrier concentration
n_{ie}	Effective intrinsic carrier concentration
N_C	Conduction band density of states
N_V	Valence band density of states
N	Net doping concentration
N_A	Acceptor concentration

N_D	Donor concentration
p	Hole concentration
$\overline{P_{abs}}$	Photon absorption probability
$\overline{P_{esc}}$	Photon escape probability
q	Electron charge
σ_n	Electron capture cross section
σ_p	Hole capture cross section
$\mathcal{R}$	Recombination rate
$\mathcal{R}_n$	Recombination rate for electrons
$\mathcal{R}_p$	Recombination rate for holes
R_s	Series resistance
S_0	Intrinsic surface recombination velocity
S_b	Back surface recombination velocity
S_E	Window/emitter interface recombination velocity
S_f	Front surface recombination velocity
S_n	Electron recombination velocity
S_p	Hole recombination velocity
T	Temperature
$\tau_{e,B}$	Electron lifetime at the base
$\tau_{e,abs}$	Minority carrier lifetime at the absorber
$\tau_{h,E}$	Hole lifetime at the emitter
τ_n	Electron lifetime
τ_{nr}	Non-radiative carrier lifetime

τ_n^{eff}	Effective electron lifetime
τ_p	Hole lifetime
τ_p^{eff}	Effective hole lifetime
τ_r	Radiative carrier lifetime
τ_{SRH}	SRH minority carrier lifetime
V_{bib}	Built-in voltage at bulk
V_{bis}	Built-in voltage at the perimeter
V_{oc}	Open circuit voltage
ϕ_i	Parameter for non-linearity in luminescent coupling evaluation
v_n	Electron thermal velocity
v_p	Hole thermal velocity
v_{th}	Carrier thermal velocity
χ	Electron affinity
χ_{eff}	Effective electron affinity
ψ	Electrostatic potential
W	Solar cell thickness
W_b	Base thickness
W_{oc}	Bandgap-voltage offset

List of acronyms

3JSC	triple junction solar sell
ARC	antireflection coating
BAC	band anticrossing
BC	boundary condition
BBT	band to band tunneling
BGN	bandgap narrowing
BSF	back surface field
BSR	back surface reflector
BCC	background carrier concentration
BOL	beginning of life
CE	collection efficiency
CPV	Concentrator Photovoltaics
CNEA	Comisión Nacional de Energía Atómica
CPV	Concentrator Photovoltaics
EL	electroluminescence

EQE	external quantum efficiency
EOL	end of life
DN	dilute nitride
DLTS	Deep Level Transient Spectroscopy
ECV	electrochemical capacitance voltage
EBIC	electron beam-induced current
IQE	internal quantum efficiency
IMM	inverted metamorphic
FCA	free-carrier absorption
FDM	Finite-Difference-Method
FEM	Finite-Element-Method
FSF	front surface field
LM	lattice matched
LC	luminescent coupling
LEO	Low Earth Orbit
LONGESST	low cost germanium substrates for next generation 4-Junction space solar cells utilising dilute nitride technology
MBE	Molecular Beam Epitaxy
MJSC	multijunction solar cell
MOCVD	Metalorganic Chemical Vapour Deposition
MOVPE	Metalorganic Vapour Phase Epitaxy
NREL	National Renewable Energy Laboratory (Golden, CO, USA)
OCC	open circuit conditions
PDE	partial differential equations

PGR	photogeneration rate
PL	photoluminescence
PR	photon recycling
QE	quantum efficiency
RTA	Rapid Thermal Annealing
RHJ	rear heterojunction
SCR	space charge region
SIMS	secondary ion mass spectrometry
S-Q	Shockley-Queessier
SRH	Sockley-Read-Hall
TAT	trap assisted tunneling
TCAD	Technology Computer Aided Design
TEM	Transmission Electron Microscopy
TMM	Transfer Matrix Method
TRPL	Time Resolved Photoluminescence
UHCPV	Ultra High Concentrator Photovoltaics
UID	unintentionally doped
VASE	variable-angle spectroscopic ellipsometry
WKB	Wentzel-Kramers-Brillouin
XRD	X-Ray diffraction

CHAPTER 1

Introduction

1.1 TCAD modelling and simulation

Modelling and simulation play a key role in the optimization and development of new semiconductor devices. To pursue the most accurate modelling of a given system, the inclusion of physical processes at the atomic-scale and their extension to large scales is required. In fact, towards a better description of the device performance, the necessity of exact solutions of a given system is desirable to provide the highest accuracy. Fig. 1.1 illustrates that as long as the time and length scale in hierarchy modelling¹ shrinks to low values (e.g. 1nm) ab-initio calculations are required to describe the physical processes at the atomic scale [Dut00]. Nevertheless, the representation of material systems at large scales requires a tremendous amount of computational resources not easily achievable with current technology. Accordingly, to solve a complex system in large scale, a combination of models in a multi-scale basis could provide a more viable solution. This requires to know the limits and capabilities of each parts in a hierarchy tool that includes all the approaches shown in Fig. 1.1. The challenge is to find appropriate linking boundaries between hierarchy levels of Fig. 1.1. This is indeed essential to cover more accurately most of the physical processes for future devices where a trend towards miniaturization (i.e. nanoscale) is already taking place.

¹The time and length scale in modelling could be thought of as the capability of modelling to capture physical processes and phenomena in time and space.

Figure 1.1: Simulation hierarchy tool. Diagram adapted from [Dut00]. The dashed rectangle indicates more recent TCAD tools.

In this thesis, the simulation of III-V multijunction solar cells (MJSC) encompasses into the class of continuum models where TCAD tools are based on partial differential equations (PDE). This has been the *work horse* for single junction solar cells and their use for multijunctions is significantly more recent.

For TCAD purposes and multijunction solar cells, there are generally different stages through which a device maker has to carry out: the proper selection of the physical microscopic mechanisms that would describe the performance of the device, how to make the device structure simpler without leaving aside important physical processes, what is the mathematical approach required, what is an appropriate discretization... and so on.

All previous stages require a very careful selection of the input parameters as well as the physical models involved. Furthermore, calibration of the TCAD models, material parameters and specific model coefficients is usually done in a very local scale which require consensus to approve/confirm the solutions. If higher accuracy is required, the proper description of device performance should be accompanied by more accurate physical models as well as an extensive involvement of different characterization techniques able to provide reliable input parameters as well as microscopic/macroscale physical quantities.

The capability of calculating the solar cell performance from fundamental material properties by solving the semiconductor governing differential equations is one of the main advantages of TCAD tools used for solar cells. This avoids the masking into one single parameter many

material features. For instance, analytical diode models involve into phenomenological parameters the recombination of the device (through the so-called saturation current or recombination pre-factor, ideality factors, etc.) while device simulators include to some extent the physics of defects, traps and so on. The quasi-neutral region is not assumed to be electric field-less and no imposed ideality factors are required. Indeed, one may be able to *predict* and correlate all outputs into the very same material parameters and model set used. Thus, there is direct correlation of parameters to physical processes. All in all, if *predictive* capabilities are pursued, the physical models employed are decisive, thus highlighting the testing of these tools either for multi-scale modelling or to provide useful insight and local solutions for experimentalists and designers.

1.2 State of the art of TCAD modelling for multijunction purposes

TCAD tools based on partial differential equations are widely used in the semiconductor field. Most of these tools approximate the solutions by solving two or more *moments*² of the Boltzmann Transport Equation (BTE). The drift-diffusion approximation (based on two moments of the BTE) has been included in many device simulation tools widely used by the PV community in the last decades (see for instance [Fos76a; CB97a]). These tools were mainly used for single junction solar cells while their implementation for multijunction purposes took longer. In fact, device simulations for multijunction solar cells started about a decade ago and its evolution has been tremendous over these years. A lot of capabilities are now included into the simulators in order to perform accurate and meaningful solutions (i.e., including non-local tunnel junction models, photon recycling, etc.) and they are continuously improving their capabilities. Although, the non-local tunnel junction models are constrained to just a few tools (mostly commercial ones, e.g., Synopsys and Silvaco), the capability of simulating full multijunction solar cells by using TCAD tools is now a reality. This was not possible until the development of such tunnel junction models [Her+08; BA10]. At that time, the integration of physics-based drift-

²"The Boltzmann transport equation can be transformed into a number of useful device equations by taking *moments* of the BTE. These *moments* are found by multiplying the equation by appropriate functions of moment and integrating over all momentum space. The first three moments yield the equations for the carrier concentration, momentum conservation and energy transport" [Col09]. The simulations of this thesis solve two moments of the Boltzmann transport equation.

diffusion solvers and non-local effects has been successfully demonstrated for multijunction solar cells [Phi+08; BA08]. Nevertheless, these physic-based models are still in their validation phase for multijunction purposes and they have not gathered full consensus in the PV community. The continuously increase of TCAD users (and tools) is beneficial, but forces to perform exhaustive testing of such tools — given the high complexity of their development — to increase the confidence on the simulation output.

All in all, the applicability of *local* models such as the drift-diffusion approximation to multijunction solar cells requires detailed study because this approximation is questionable when the whole potential profile experienced by the carriers is important (non-local effects). This is the case of devices operating in the nm-range where non local effects and quasi-ballistic transport increase their relevancy. In these cases, more than two moments of the Boltzmann transport equation can be solved to derive the so-called hydrodynamic models where the heat flux equation is now included into the given set of semiconductor equations to consider for example, self-heating, saturation velocity, and other effects. III-V multijunction solar cells typically range their size in some mm^2 with subcell active thicknesses of about $1\text{ }\mu\text{m}$ or thicker, thus the effect of feature size may not drive the performance, albeit it has not been determined yet. There are, however, some structures and regions that explicitly require more complex models than drift-diffusion approximation to consider non-local and quantum effects. For instance, this is the case of tunnel junctions and it could be the case for isotype³ or anisotype² heterojunctions widely used in multijunction solar cells. Accordingly, drift-diffusion solvers as well as non-local models have been extensively used in all simulations performed along this thesis in order to examine, test and extend the use of device simulations in the multijunction solar cells field. Furthermore, they will be used for the detection of their main capabilities and limitations.

1.3 Objectives

III-V multijunction solar cells already exhibit very high conversion efficiencies both for space or Concentrator Photovoltaics (CPV) applications. Presently, MJSC show a rate of increasing efficiency higher than the majority of PV-technologies, perhaps with the exception of perovskite-based devices. These high efficiencies directly translate into a reduction of the area of devices, thus the size of the CPV system and ultimately the cost. Although cost is still higher than other

³Isotype involves the use of materials with the same doping polarity, while anisotype refers to the ones with different doping polarity.

PV technologies (i.e. Silicon technology), measured efficiencies under concentrated light above 46% have been already achieved and pathways in short-term to reach the barrier of 50% at the device level and the 40% at the module level envisage the possibility of using multijunction solar cells as an important technology to deliver large-scale electricity [Fri+13; Phi+15]. For space applications, efficiencies at 1-sun spectrum about 30% have been already demonstrated and short-term targets multijunction devices with more than 33% [Sua+17]. Although excellent devices have been already demonstrated, technical improvements at the system and solar cell level must still be attained to surpass the current efficiencies.

In order to understand the main limiting mechanisms and to propose alternatives for new and/or optimized structures, this thesis focuses on the device level and covers the device simulation, characterization and examination of different multijunction solar cells for space and high-concentration terrestrial applications. Most of the simulations of multijunction solar cells has been performed under the framework of commercially available TCAD software (Atlas) from Silvaco company. All simulations are performed with strong focus on their validation with experimental data by using a single set of material parameters and models (unless specified) for dark and illuminated conditions. To our knowledge, this has not been tackled in the past to the same extent that has been carried out within this thesis.

Accordingly, this thesis faces the following general objectives:

1. To build a TCAD modelling framework for the analysis of the individual components of multijunction solar cells, including individual subcells and tunnel junctions.
2. To build a TCAD modelling framework for the analysis of triple and quadruple junction solar cells.
3. To develop a simulation platform able to guide the design of devices, the design of experiments as well as to optimize and improve the solar cells manufactured at the IES-UPM.
4. To increase the confidence of simulation results coming out from TCAD simulators.
5. To contribute to the understanding of state-of-the-art multijunction solar cells by means of advanced characterization and modelling which results in the insight of their limiting mechanisms in order to propose further efficiency improvements.

1.4 Thesis outline

This thesis is outlined as follows:

- Chapter 2 is devoted to the description of the models used in a TCAD environment with the ultimate goal of simulating multijunction solar cells for terrestrial and space applications, namely GaInP/GaInAs/Ge and GaInP/GaInAs/dilute nitride/Ge. Here we include the fundamentals, main assumptions, particularities and description of the simulation framework employed.
- Chapter 3 presents the TCAD simulation, characterization and analysis of the individual subcells of a multijunction solar cell GaInP/GaInAs/Ge and other components such as tunnel junctions GaAs/GaAs, AlGaAs/GaAs, GaInP/AlGaAs where non-local tunnel junction models have been applied and calibrated.
- Chapter 4 shows the study and comprehensive macroscopic validation of the multijunction model for a 3J solar cell (GaInP/GaInAs/Ge). Additionally, a couple of case studies for this structure are presented: 1) the exploration of the potential use of this structure at ultra-high concentration and 2) the performance of concentrator 3J structures upon proton irradiation for space applications.
- Chapter 5 exposes the study and comprehensive macroscopic validation of dilute nitride single junction solar cells and its incorporation into a 4J solar cell (GaInP/GaInAs/dilute nitride/Ge). The requirements of the dilute nitride subcell are assessed. The limitations and possible pathways to the enhancement of germanium solar cells for 4J structures are examined. Finally, efficiency calculations based on practical values are carried out for a 4J structure.
- Chapter 6 deals with the influence of temperature on the luminescent coupling of very high quality multijunction solar cells (GaInP/GaAs and GaAs/GaInAs tandems) by means of experimental and theoretical investigations. This examination demonstrated the reduction of LC with temperature which is useful information for a better design and optimization of multijunction solar cells at operating temperatures in CPV applications.
- Chapter 7 includes the main future works.
- An Appendix containing a review of the material parameters obtained from the literature as well as those characterized within this work and the ones derived from the data fitting

procedures. The materials are mainly those satisfying lattice matching condition to GaAs and Ge such as: GaInP, GaAs, AlGaAs, GaInAs, AlGaInP, AlInP, Ge and dilute nitrides such as GaNAsSb.

1.5 Framework

The present thesis has been carried out at the *Instituto de Energía Solar* (IES-UPM) facilities in Madrid under the workload of the III-V Semiconductors Group. A significant amount of work was performed within the framework of several national and international scientific projects and collaborations with academic institutions as well as industry partners and research centres. The III-V Semiconductors Group covers the whole life-cycle chain of multijunction solar cells including their manufacturing, characterization, simulation and reliability intended to operate in space or at very high concentrations. The work of this thesis is focused on the characterization and simulation aspects.

All the TCAD work was mainly developed at the IES-UPM. Thanks to the III-V Semiconductors Group, I had access to numerous fabricated III-V solar cells to compare with all simulations presented here. Furthermore, I had the opportunity to be deeply involved in the characterization techniques used in the group. An important part of the philosophy in our group is to keep simulations close to practical devices, so that they could help to detect the main limiting mechanisms as well as to propose realistic, optimized or new designs guiding the manufacturing of improved solar cells.

The research on dilute nitrides was performed within a European project called *LONGESST* where the role of the III-V Group was devoted to the fabrication, characterization and design of multijunction solar cells. I had contributed mostly to the simulation, design and device characterization of the devices.

Moreover, I participated in proton irradiation of single and triple junction solar cells carried out within a strong collaboration with the CNEA in Buenos Aires, Argentina, under a scientific collaboration devoted to the study of III-V based solar cells.

Finally, the research on luminescent coupling was mainly developed at NREL facilities in Golden, Colorado, USA as a result of a short research stay. All the experimental work was performed by the author of this thesis. I had also used the LC models developed at NREL and included temperature dependences in the diode models for the analysis. Apart of the LC work, other subjects of this thesis were additionally enriched by several characterization activities performed at NREL.

CHAPTER 2

TCAD simulation of multijunction solar cells: Fundamentals overview

In this chapter, an overview of the physical models and basic concepts of TCAD modelling to simulate the optoelectronic performance of multijunction solar cells is presented. Firstly, the simulation environment and the fundamental semiconductor equations, boundary conditions and drift-diffusion models together with quantum models are described with emphasis on multijunction structures. Then, particularities of the simulation framework, assumptions and limitations are recalled. Finally, the assumptions used for the comparison of the resulting 2D simulations with experimental data (3D) as well as the data fitting procedure are explained.

Many semiconductor problems can be approximated by solving the governing equations inside a simulation domain that is divided into sub domains connected by nodes and forming a mesh [Sel84]. At the nodes, partial differential equations can be solved by simpler algebraic methods. To this purpose, Finite-Difference-Method (FDM) and Finite-Element-Method (FEM) are widely used for the partitioning of a given semiconductor structure. A TCAD environment usually includes: FEM (or FDM) with algorithms for mesh generation (either manual or automatic) and solvers for the governing equations interacting with the system through properly defined boundary condition (BC) in order to provide a solution for electrical, optical or thermal problems (the so-called device simulations). Additionally, a TCAD environment also provides the possibility to perform simulations in 2D or 3D not only at the device level, but also at the process level [Sel84; Sil16] (see Fig. 2.1).

Figure 2.1: Device simulation sequence involving general stages on the design of semiconductor devices by using TCAD. Diagram adapted from [VG02]

A process simulation enables the analysis of different variables in the manufacturing process of a semiconductor device, i.e., etching, oxidation or deposition processes, p-n junction formation, etc. For instance, it is useful in the optimization of the semiconductor fabrication process or the prediction of dopant profiles, to name a few features. In this thesis, all the TCAD simulations performed are related to device simulations and this is where we will focus most of the attention. Accordingly, in order to perform a given simulation the following stages must be followed:

1. Semiconductor structure definition: mesh construction and region definition.
2. Material properties definition: band parameters, carrier properties, refractive index, etc.
3. Setting boundary conditions: ohmic/Schottky contacts, interface recombination and transport models for heterojunctions interfaces, etc.
4. Model selection: Fermi-Dirac statistics, recombination models, mobility models, quantum models, etc.
5. Choosing a numerical method (and related parameters): Gummel, Newton, Block, etc.

6. Defining the operating conditions: light, dark, etc.

FEM is the general discretization procedure employed by our simulation framework to construct a mesh within a structure where all models will be solved. For multijunction solar cells, two explicit different meshes (one for the structure and an additional one for tunnel junctions) and several boundary conditions are required. This is illustrated in Fig. 2.2.

Figure 2.2: Cross-section general scheme of a double junction solar cell structure (not to scale) showing the non-uniform background mesh and the region occupied by the secondary mesh required for tunnel models. ARC (violet), GaAs contact layer (green), top cell (blue), tunnel junction (gray), bottom cell (red) and electrodes (gold) are depicted. Boundary conditions indicated by arrows are extended along x-direction

Due to the lateral current flow imposed by the front metal grid, a strong non-uniform mesh is mandatory not only along the depth but also in the x-direction. For instance, let us consider light normally impinging to the front surface of the structure shown in Fig. 2.2. In this case, there will be regions that will generate a significant amount of electron-hole pairs (at the illuminated side) and other regions where no electron-hole pairs generation is taking place (dark region beneath the front electrode). This implies a very high difference in minority carrier concentration could be found at the vicinity of the contact and along the depth of the structure. In order to capture this strong carrier density variation, a finer mesh must be considered. Accordingly, notice that at the interface between dark (below the front contact) and illuminated regions, the density of mesh points increases gradually in order to properly resolve charge variations in space. This will also apply to p-n junctions, interfaces, etc. as illustrated in Fig. 2.2.

In order to design a suitable mesh, different strategies can be followed. First, it can be considered that the mesh size is limited by the Debye length (D_L) which can be calculated ac-

according to: $D_L = \sqrt{\frac{\epsilon k T}{N q^2}}$ [Tom93; VG02], where N is the doping density. For instance, for a doping concentration of 10^{19} cm^{-3} the Debye length ranges between 1.3-1.5 nm for GaInP, GaAs and Ge. Therefore, the mesh resolution should be below these values in regions where charge variations in space must be resolved. Another different strategy is to find the solution in a first run and detect regions where strong charge variations occur (either manually or automatically¹) and refine the mesh density accordingly. In some other cases, it is also reasonable to define a suitable mesh and optimize it by increasing the mesh points until no significant changes occur in the output results.

Heretofore, we have briefly described some general concepts about *meshing* or *gridding* which correspond to stage one previously listed in Fig. 2.1. Stages 2 to 6 (not sequentially), which involve the interaction between semiconductor equations, boundary conditions and the selected models for a multijunction solar cell structure (like that of Fig. 2.2) will be reviewed and described.

2.1 Semiconductor equations

A set of semiconductor equations has been derived from Maxwell's laws results in the Poisson (Eq. 2.1) and continuity equations for electrons and holes (Eqs. 2.2 and 2.3) [Van50]. These equations relate the electrostatic potential with the carrier densities in a semiconductor device. While the variation in electrostatic potential due to local charges is considered via Poisson equation, the continuity equations describe how the electrons and holes accommodate while being subjected recombination and generation processes.

$$\nabla \cdot (\epsilon \nabla \psi) = q(n - p - N_D^+ + N_A^-), \quad 2.1$$

$$\frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot \vec{J}_n + G_n - \mathcal{R}_n, \quad 2.2$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \nabla \cdot \vec{J}_p + G_p - \mathcal{R}_p \quad 2.3$$

This set of three coupled partial non-linear differential equations is the general framework for any device simulation that enables the calculation of the carrier densities and electrostatic

¹Some simulators include automatic *meshing* or *regridding* procedures that perform an initial solution in order to detect charge variations and increase progressively the mesh points at those regions.

potential². Auxiliary equations are also required to determine the current flow ($\vec{J}_n$ and $\vec{J}_p$) and the generation/recombination terms for specific models. In the particular case of simple solar cell structures, drift-diffusion equations for electrons and holes (Eqs. 2.4 and 2.5) are normally effective to describe the current transport within the device:

$$\vec{J}_n = q\mu_n n \nabla \psi + qD_n \nabla n, \quad 2.4$$

$$\vec{J}_p = q\mu_p p \nabla \psi - qD_p \nabla p \quad 2.5$$

Drift-diffusion equations are obtained by solving two moments of the Boltzmann transport equation (BTE)³. The current density at a given point in the structure of the device depends on the carrier concentration and the electric field calculated at the same point. Therefore, this model is normally referred to as a *local* model and it is one of the most important features of drift-diffusion models typically considered in TCAD environments. This, indeed, allows to introduce one of the most powerful concepts of this approximation: the continuity concept. The continuity concept implies that the current density at a given point x_1 is equal to that at point x_2 (where $x_2 > x_1$) in steady-state conditions unless particles are increased or lost by generation or recombination [Fon10]. In other words, continuity equations are based on conservation laws which implies that the same amount of energy at the input of an element would exist at the output of it. Mathematically, for the steady-state integral form, this means that:

$$J_n(x_2) = J_n(x_1) + q \int_{x_1}^{x_2} G_n(x) dx - \int_{x_1}^{x_2} \mathcal{R}_n(x) dx \quad 2.6$$

These concepts are the basis to understand the most general device physics conditions considered in drift-diffusion models. Usually, we are interested only in the steady-state conditions and the *local* behavior is normally valid to our purposes in the modelling of simple solar cell structures.

In order to solve this set of partial non-linear differential equations (Eqs. 2.1 to 2.5), numerical methods are required because it is not possible to obtain a direct solution in one step. Gummel et al. introduced in the 1960s an iterative procedure allowing the numerical solution of carrier densities (n and p) in transistors operating at different conditions [Gum64]. It was not

² ψ, n, p is the natural variable formulation while some other approximations use quasi-Fermi levels or Slotboom formulations. Depending on the kind of simulation (transient or steady-state) one or another is preferred. See more details on [VG02]

³The first moment involves the carrier concentration equation, the second moment involves that of moment conservation equation and a third moment is related to the energy balance equation.

until the 1970s that this simulation code was applied for the first time to the study of solar cells demonstrating its prediction capabilities to further increase the efficiency of silicon solar cells [Fos76b]. Nowadays, sophisticated numerical techniques and robust iteration strategies such as the Gummel, Newton and block-Newton, and some others have been developed and they are widely available in most simulators [Sil16]. In fact, Newton's method is the one that is applied to most of the simulations performed here (unless specified), being able to reach convergent solutions in a fast and accurate manner.

2.2 Carrier statistics

Electrons in thermal equilibrium at a given temperature (T) in a semiconductor lattice follow Fermi-Dirac statistics. The probability of an available electron state with energy ε being occupied by an electron is:

$$f(\varepsilon) = \frac{1}{1 + \exp\left(\frac{\varepsilon - E_F}{kT}\right)} \quad 2.7$$

where E_F is a spatially independent reference energy known as the Fermi level and k is the Boltzmann constant. In the limit that $\varepsilon - E_F \gg 1$, a simplification can be done and the probability $f(\varepsilon)$ calculated as:

$$f(\varepsilon) = \exp\left(\frac{E_F - \varepsilon}{kT}\right) \quad 2.8$$

Boltzmann statistics (2.8) are generally accepted in semiconductor device theory, however, it is largely questioned when dealing with highly-doped devices (degenerated) as typically found in materials for multijunction solar cells. Accordingly, all simulations performed here follow Fermi-Dirac statistics.

2.2.1 Effective density of states

Integrating the carrier statistics over a parabolic band density of states in the conduction and valence bands, whose minimum energy is located at energies E_C and E_V respectively, results in the following expressions for electron and hole concentrations:

$$n = N_C \mathcal{F}_{1/2}\left(\frac{E_F - E_C}{kT}\right), \quad 2.9$$

$$p = N_V \mathcal{F}_{1/2}\left(\frac{E_V - E_F}{kT}\right) \quad 2.10$$

The Fermi-Dirac integral is then defined as:

$$\mathcal{F}_{1/2}(\eta) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{1 + \exp(\varepsilon - \eta)} \quad 2.11$$

where

$$\varepsilon = \frac{E - E_C}{kT}, \quad 2.12$$

$$\eta = \frac{E_F - E_C}{kT} \quad 2.13$$

The quantities n, p are usually expressed in terms of the Fermi-Dirac integrals, where $\mathcal{F}_{1/2}$ is the integral of the order of 1/2. Then, the effective density of states for conduction and valence bands is given by:

$$N_C(T) = 2 \left(\frac{2\pi m_e^* kT}{h^2} \right)^{3/2}, \quad 2.14$$

$$N_V(T) = 2 \left(\frac{2\pi m_h^* kT}{h^2} \right)^{3/2} \quad 2.15$$

The carrier concentration can be also expressed in terms of intrinsic carrier concentration. Accounting for Fermi-Dirac statistics, this can be written as:

$$n_i = \sqrt{N_C N_V} \mathcal{F}_{1/2}(\eta) \mathcal{F}_{1/2} \left(\frac{-E_g}{kT} - \eta \right) \quad 2.16$$

2.3 Bandgap narrowing

One of the consequences due to heavy doping (as usual in many layers of a MJSC) is bandgap narrowing (BGN). BGN results from many-body effects and potential fluctuations of free carriers. The many-body effects describe the interaction of free carriers. This means that all effects are usually encompassed as an effective reduction of the bandgap of the material. Physically, carrier-carrier or carrier-ionized impurity interactions occur via long-range coulombic interactions and via their spin. As doping concentration increases, the free carrier concentration redistributes in order to reduce those interactions, thus reducing the total energy of the system. It can be also understood by the appearance of an impurity band close to the valence or conduction band that evolved by the overlapping the wave functions of impurity atoms with localized carriers [Sch98].

In device modelling, the BGN is typically included into the calculation of the intrinsic carrier concentration as an effective reduction of the bandgap which usually follows a logarithmic

dependence with doping concentration. Indeed, simple expressions are usually derived from conventional semiconductors enabling the possibility of including directly the BGN into numerical simulators (see for instance [JR91] and references therein).

There are, however, a couple of concerns: 1) the carrier statistics used in the derivation of BGN and 2) the distribution of the narrowing between bands. The intrinsic carrier concentration would be affected differently depending on the carrier statistics used in the BGN derivation. Device simulators typically use a correction factor which is the difference of the Fermi energy level between the calculation performed by employing Boltzmann and Fermi-Dirac statistics [Shi+03; LNC07]. Additionally, almost all empirical models typically apply the shifting of the band to be distributed by 50/50 among the valence and conduction band edge. Nevertheless, the distribution can occur independently of the dopant type and unequally between bands mainly because potential fluctuations act on both electrons and holes differently. The simulator used here (Silvaco-Atlas) directly applies all ΔE_g to the minority band.

The effects of BGN are included into the simulator through an effective reduction of the bandgap typically extracted from empirical models and literature. The analytical expressions used depend mostly on the material, thus more information can be found in Appendix A. In most materials used for multijunction solar cells, expected ΔE_g is about some meV up to hundreds of meV for the highest doping concentrations ($\sim 10^{20} \text{cm}^{-3}$). The bandgap shrinkage inherently implies that the intrinsic carrier concentration would be modified as follows:

$$n_{ie}^2 = n_i^2 \exp\left(\frac{\Delta E_g}{kT}\right) \quad 2.17$$

Finally, ΔE_g is also applied partially to the electron affinity of the material. Therefore, an effective electron affinity is calculated by means of:

$$\chi_{eff} = \chi + \Delta E_g \cdot f_{asym} \quad 2.18$$

where f_{asym} is the calibration parameter that determines the fraction of ΔE_g that is applied to χ_{eff} .

2.4 Carrier generation-recombination models

Heretofore, we have described how carrier densities and electrostatic potential are calculated and how an auxiliary set of drift and diffusion equations helps determine the current flow across the device. It is still pending to determine some parameters such as those that involve generation and recombination processes which are dependent on the specific models used for their

calculation. These parameters are typically used in the multijunction solar cell modelling in a modular fashion. One can directly neglect them or consider these parameters by using different physical models. For instance, generation processes such as those regarding light absorption — and light emission and re-absorption (photon recycling)— could be self-consistently included into the generation term of Eqs. 2.2 and 2.3. On the other hand, conventional recombination such as radiative and non-radiative processes could be also considered via the recombination terms of Eqs. 2.2 and 2.3. Additionally, the tunnel junction current transport is implemented via an injected current while the trap assisted tunneling accounted for through a recombination term (in the form of SRH equation) by including appropriate enhancement factors (see section 2.8). Accordingly, in this section the photogeneration calculation as well as the recombination processes considered for multijunction solar cell modelling are described.

2.4.1 Photogeneration

Fonash describes in his book up to 6 processes in solar cells related to absorption of light [Fon10]. Here, five of those six processes could be applicable to III-V materials⁴. For instance: 1) free carrier absorption within a single band (intraband processes), 2) absorption between gap states and gap states and a band, 3) phonon absorption (electrons not involved), 4) exciton-producing absorption and 5) band to band transitions. While some of those processes could induce electron-hole generation, some others do not. Indeed, only considering band to band absorption which promotes free electron-hole generation is a very reasonable assumption for III-V semiconductors. Accordingly, hereinafter the photogeneration process will be referred to as a process where absorption directly leads to electron-hole generation (unless explicitly noted).

Nowadays, there are several approximations that enable the calculation of the photon flux as a function of the position within a given structure. Most of their differences rely on their fundamental derivations and assumptions made. Usually, these calculations start from the refractive index of the materials that are typically obtained from the literature. One of the advantages of TCAD simulators is that they can include new models in a modular fashion. Indeed, it may be convenient to calculate externally the photogeneration to create the associated files that can then be included into the simulator as an extra generation term to couple the optical and electric transport solutions. In some cases, it could be advantageous to avoid optical calculations within a FEM-based environment that is mesh-dependant, more problematic and slower. Furthermore,

⁴We intentionally obviate the process related to amorphous materials.

it provides higher degree of flexibility for the inclusion of different optical approaches into the simulator. Table 2.1 shows some of the optical methods typically used for solar cell and summarizes their potential use and main features.

For planar structures such as the ones used within this thesis and under the assumption that material optical properties are extended uniformly along their volume (i.e. constant refractive index in the whole material region, position-independent), the Transfer Matrix Method (TMM) (and its variants) is an excellent tool to calculate the photon flux in a solar cell. It is fast, accurate and capable of including interference effects typically found in multijunction solar cells where many layer thicknesses are in the range of the incident wavelength. Accordingly, TMM is the approach used in this thesis. It is indeed, well known that TMM provides excellent results for planar structures as it will be demonstrated along this thesis. Notwithstanding, more sophisticated approaches (or modified-TMM) are required if one intends to model different optical systems such as multijunction solar cells with graphene monolayers [Bar17], periodic gratings, textured surfaces, or those including nano structures that may act as outstanding anti reflection coatings [Bue+15], as well as photonic and ad-hoc structures for maximizing light trapping [Mel13]. All the methods shown in table 2.1 can be coupled with most of the TCAD environments available.

Since the TMM and its variants is extensively detailed in many articles, textbooks, etc. (see for instance [BW94; Pra01b; Pre99; KS02; Cen05; Sil16]), we will only focus here in the main aspects related to solar cells and its applicability to the structures studied. Accordingly, the photogeneration rate is calculated by:

$$PGR(y) = \frac{\lambda}{hc} \alpha \frac{|E(y)|^2}{2\eta} \quad 2.19$$

where $E(y)$ is the electric field at any point y within a certain layer calculated with TMM and α the absorption coefficient of the material. In this case, η^5 is assumed to be equal to 1 which means that every photon absorbed generates an electron hole pair, unless free-carrier absorption is taken into account.

How to deal with the thick substrate of typical multijunction solar cells in TMM calculations deserves attention. On the one hand, a thick layer such as the substrate (hundreds of micrometers) can be typically modeled as an incoherent layer, i.e., the electric field wave is only tracked in intensity while neglecting its phase. In other words, the reflected wave at the back of the

⁵Notice that the use of η in Eq. 2.19 is not related to the efficiency of a solar cell neither the quantity described in section 2.2.1

Table 2.1: Summary of some of the typical methods for photo generation calculation in solar cells. BPM stands for beam propagation method, RCWA for rigorous coupled-wave analysis and FDTD for finite difference time domain analysis.

Method	Basis	Features	Application	Computation
Raytracing	Geometric optics	Robust No coherent effects	Geometric optics	High
BPM	Solves a more general Helmholtz wave equation Based on paraxial approximation	Diffraction and coherent effects considered	No periodic structures in x-direction	High
TMM	Matrix relating total tangential components of the electric and magnetic fields at multilayer boundaries	Fast, accurate Coherent effects no textured interfaces no gradual changes	Multilayer systems Thin-film planar structures.	Low
Modified-TMM	TMM for specular light and raytracing for diffuse light	Coherent/incoherent effects diffusive light inclusion	Textured surfaces Graded interfaces	Medium
FDTD	Solves for the electric and magnetic field propagation directly from the fundamental wave equations	Includes reflection diffraction and coherent effects	Non-planar structures Sub and nanometer-range	High
RCWA	Fourier-space method	Diffraction structures.	Non-planar structures Sub and nanometer-range	High

substrate in the TMM is equal to zero. On the other hand, the present model included into the simulator treats all waves as coherent while the substrate (or the last layer in the stack) can be treated as a semi-infinite layer. In this case, the difference between these two approaches will appear at the layers below the substrate, i.e., the back metallization. To our purposes, neglecting the optical behavior of the metal is sufficient and we later demonstrate that the semi-infinite approach is able to reproduce quite well the optical behavior of the solar cells studied in this thesis. Indeed, this is supported by the fact that the influence of the back metallization (as a possible back surface reflector (BSR) and neglected by the model) has negligible impact on the solar cell performance mainly because of one fundamental factor: highly doped germanium (such as the one used here) shows strong FCA (see [NSM15] and references therein) and absorbs a high amount of photons with low energies (<0.8 eV), lowering the reflectance at the rear metal. This reason justifies the negligible impact of the metal on these structures; however, it is worth to mention that if FCA could be diminished up to a point that can be insignificant (e.g., by using lower doped substrates [Fer+07; Hoh+10]) and high reflection properties are achieved at the metal, the inclusion of incoherent layer treatment and free-carrier absorption effects is a must to accurately describe the optical behavior of the surface/metal interface, especially at low energies. Furthermore, the necessity to deal with incoherent layers would also be part of the modelling of alternative architectures, for instance the GaInP/Si tandem that contains a thick glass between GaInP and Si [Ess+15].

2.4.2 Radiative recombination

Radiative recombination may be accounted for by using the expression:

$$\mathcal{R}_{rad} = B(np - n_i^2) \quad 2.20$$

where B is the radiative recombination coefficient. More details, literature values and the ones extracted from data fitting are listed in Appendix A)

2.4.3 S-R-H recombination

Semiconductor materials exhibit crystal defects that can be caused, for instance, by impurities in the material or dangling bonds at the interface or surface. These defects can act as recombination centres or traps affecting the carrier recombination within the device. Traps are located within the energy bandgap and they exchange carriers with either the valence or the conduction band. As a result, the space charge in a semiconductor (either bulk or interface) gets modified

as well as the recombination statistics. In the case of interface (or surface) it is usually modelled as a sheet of charge at the interface and therefore is controlled by the interface boundary condition (see section 2.4.5). The amount of charge is typically calculated by appropriate emission and capture rates of these defects whose values are dependent on the defect properties (i.e., energy level, capture section coefficients, density, distribution...). Indeed, the trap-model that will be explained here takes into account that carriers are being emitted or captured by donor or acceptor-like traps lying in the forbidden gap. This interaction exchanges charge between conduction and valence bands, so the charge density at the surface is modified according to:

$$\text{div}(\epsilon \nabla \psi) = q(n - p - N_D^+ + N_A^- + N_{tD}^+ - N_{tA}^-) \quad 2.21$$

where ψ is the electrostatic potential, ϵ the local permittivity, N_D^+ and N_A^- are the densities of ionized donor and acceptor impurities respectively, N_{tD}^+ , N_{tA}^- are the ionized trap density for donors and acceptors and the other variables have their usual meaning. The ionized trap densities depend upon the trap density, N_{tD} and N_{tA} , and their probability of ionization, F_{tD} and F_{tA} . For donor-like and acceptor-like traps respectively, the ionized densities are: $N_{tD}^+ = N_{tD} \cdot F_{tD}$ and $N_{tA}^- = N_{tA} \cdot F_{tA}$.

The probability of ionization assumes that the capture cross sections are constant for all energies in a given band and follows the analysis developed by Simmons and Taylor [ST71]. The initial occupancy of traps is calculated by the following equations for acceptor and donor-like traps.

$$F_{tA} = \frac{v_n \sigma_n n + e_{pA}}{\nu_n \sigma_n n + \nu_p \sigma_p p + e_{nA} + e_{pA}} \quad 2.22$$

$$F_{tD} = \frac{v_p \sigma_p p + e_{nD}}{\nu_n \sigma_n n + \nu_p \sigma_p p + e_{nD} + e_{pD}} \quad 2.23$$

where σ_n and σ_p are the carrier capture cross sections for electrons and holes, respectively and ν_n and ν_p are the thermal velocities for electrons and holes. The probability of ionization (equations 2.22-2.23) is the electron-hole concentration to the total carrier concentration ratio which is determined by the electron emission rate e_{nD} and the hole emission rate e_{pD} . For donor-like traps, the electron and hole emission rates are defined by:

$$e_{nD} = \frac{1}{g} v_n \sigma_n n_i \exp\left(\frac{E_t - E_i}{kT}\right) \quad 2.24$$

$$e_{pD} = g v_p \sigma_p n_i \exp\left(\frac{E_i - E_t}{kT}\right) \quad 2.25$$

where g is the degeneracy factor of the material, n_i the intrinsic carrier concentration, E_t the trap energy level, E_i the intrinsic Fermi level and the other variables have their usual meaning.

For acceptor like traps, the term e_{nA} and e_{pA} are the electron and hole emission rates defined by:

$$e_{nA} = g v_n \sigma_n n_i \exp\left(\frac{E_t - E_i}{kT}\right) \quad 2.26$$

$$e_{pA} = \frac{1}{g} v_p \sigma_p n_i \exp\left(\frac{E_i - E_t}{kT}\right) \quad 2.27$$

The above equations help us define the charge density at the surface and how it modifies the carrier concentration. This modification is implemented in the recombination term for both carrier types as:

$$\mathcal{R}_{SRH,n} = \frac{np - n_i^2}{\tau_n [p + g \cdot n_i \exp(\frac{E_i - E_t}{kT})] + \tau_p [n + \frac{1}{g} n_i \exp(\frac{E_t - E_i}{kT})]} \quad 2.28$$

for donors and

$$\mathcal{R}_{SRH,p} = \frac{np - n_i^2}{\tau_p [n + \frac{1}{g} n_i \exp(\frac{E_t - E_i}{kT})] + \tau_n [p + g \cdot n_i \exp(\frac{E_i - E_t}{kT})]} \quad 2.29$$

for acceptors. The carrier lifetime $\tau_{p,n}$ is derived from the defect density and is equal to $\tau = (\sigma \nu_{th} N_t)^{-1}$. Here N_t is the trap density, ν_{th} the carrier thermal velocity and σ the capture cross section. The recombination terms are added to the carrier continuity equations in order to solve self-consistently the semiconductor fundamental equations to calculate dark I-V curves.

$$\mathcal{R}_{SRH} = \frac{np - n_i^2}{\tau_n [n + n_i \exp(\frac{E_i - E_t}{kT})] + \tau_p [p + n_i \exp(\frac{E_t - E_i}{kT})]} \quad 2.30$$

2.4.4 Auger recombination

Auger recombination may be accounted for by using the expression:

$$\mathcal{R}_{Auger} = C_n (pn^2 - nn_i^2) + C_p (np^2 - pn_i^2) \quad 2.31$$

where C_n and C_p are the Auger coefficients for electrons and holes.

2.4.5 Surface recombination

To model surface or interface recombinations between two given materials, different approximations could be followed.

1. Set a fixed surface/interface recombination velocity.

2. Specify surface/interface traps lying at a specific energy level (or levels) and being able to interact with electrons from the conduction band (acceptor) or with holes in the valence band (donor), and setting the corresponding capture coefficients and trap densities in order to derive an effective surface recombination velocity, as already explained in section 2.4.3.
3. Set a fixed positive or negative surface charge density: Q_t .

Due to the discretization of the structure, the effective carrier lifetimes are unavoidably dependent on the geometry of the structure and the given mesh surrounding the interface. This ensures that the recombination at surface only exists exactly at the surface. Accordingly, the effective carrier lifetimes for electrons and holes are given by:

$$\frac{1}{\tau_n^{eff}} = \frac{1}{\tau_n^i} + \frac{d_i}{A_i} S_n, \quad 2.32$$

$$\frac{1}{\tau_p^{eff}} = \frac{1}{\tau_p^i} + \frac{d_i}{A_i} S_p \quad 2.33$$

$\tau_{n,p}^i$ is the bulk carrier lifetime calculated at node i along the interface, d_i and A_i are the length and area of the interface for node i according to box discretization definitions. The S_n and S_p parameters are the recombination velocities for electrons and holes, respectively.

2.5 Carrier mobility

Electrons and holes are accelerated by electric fields, but they lose momentum associated to several scattering mechanisms. The dominant scattering mechanisms are those related to lattice vibrations (phonons), impurities, carrier-carrier interactions, surfaces and other crystal imperfections. All these microscopic phenomena are enclosed in a single parameter as the carrier mobility that depends on the local electric field, doping concentration, lattice temperature, etc. Mobility modelling is usually categorized into: a) low-field behavior, b) high-field behavior, c) bulk semiconductor regions and d) inversion layers.

Low-field mobility is characterized by carriers that are almost in equilibrium with the lattice, and the mobility have a characteristic value denoted by μ_{p0} and μ_{n0} , for holes and electrons, respectively. These values are mainly affected by phonon (i.e., temperature) and impurity scattering (i.e., doping concentration). This is the behavior that is usually applied to bulk regions in the simulation of most component-materials of multijunction solar cells.

As carriers are accelerated in an electric field, their velocity begins to saturate when the electric field magnitude becomes significant. Thus, carriers that gain energy are now able to be involved in additional scattering processes. This is referred to as the high-field behavior category and results in a diminution of the drift velocity, which no longer increases linearly with the electric field, and it is accounted for by an effective reduction of the low-field mobility. These two categories of mobility modelling are the ones that have been applied in the simulation of multijunction solar cells.

The low-field mobility is usually modelled by the well-known expression by Caughey & Thomas [CT67]. In the particular case of III-V semiconductors an excellent reference is that of Sotoodeh et al. [Sot+00], although it is important to recall that Sotoodeh makes no distinction between minority and majority carrier mobility. Because mobility is very dependent on the material, it will be described in more detail in Appendix A.

In some cases, the high-field behavior is included into the simulations. This is implemented by using the Caughey & Thomas expressions:

$$\mu_n(E) = \mu_{n0} \left[\frac{1}{1 + \left(\frac{\mu_{n0} E}{v_{sat,n}} \right)^{\beta_n}} \right]^{1/\beta_n}, \quad 2.34$$

$$\mu_p(E) = \mu_{p0} \left[\frac{1}{1 + \left(\frac{\mu_{p0} E}{v_{sat,p}} \right)^{\beta_p}} \right]^{1/\beta_p} \quad 2.35$$

where E is the parallel electric field, β_n and β_p are the input coefficients while μ_{n0} and μ_{p0} are the low-field electron and hole mobilities, respectively. The use of Eqs. 2.34 and 2.35 adds additional complexity for numerical convergence. Depending on the context, it may be more practical to neglect it. See Appendix A for details about the input parameters for several material.

The mobility in dilute nitrides deserves special mention. It is well known that the introduction of minute amounts of nitrogen into III-V materials results in a large decline of electron mobility [VR07]. As a consequence of the host-nitrogen interaction, the conduction band splits and becomes highly non-parabolic, which results in a strong influence in the transport properties. Section A.2.1 provides more details and results on the Hall mobility characterization of this material.

2.6 Thermionic and thermionic field emission

Thermionic emission mechanism of carrier transport allows electrons to be transferred from an allowed state in one side of an interface to an allowed state on the other side of the interface. This occurs, ideally, with no change in total energy. In general, the current flow over a barrier between two semiconductors is described by (see [YEH93] and references therein):

$$\vec{J}_n = q(1 + \delta) (\nu_{n+}n^+ - \nu_{n-}n^-) \exp\left(\frac{-\Delta E_C}{kT}\right), \quad 2.36$$

$$\vec{J}_p = (q)(1 + \delta) (\nu_{p+}p^+ - \nu_{p-}p^-) \exp\left(\frac{-\Delta E_V}{kT}\right) \quad 2.37$$

where J_n and J_p are now the electron and hole current densities, n^+ , n^- , p^+ , p^- and ν_{n+} , ν_{n-} , ν_{p+} , ν_{p-} are the electron and hole densities as well as the electron and hole thermal velocities at each side of the heterointerface (details on these two quantities are given in [HY90; YEH93]). δ corresponds to the tunneling factor if thermionic field emission is considered. This factor takes into consideration the transmission probability of a carrier across the barrier by using one-dimensional Wentzel-Kramers-Brillouin (WKB) approximation. δ is then calculated as:

$$\delta = \frac{1}{kT} \int_{E_{min}}^{E_C^+} \exp\left(\frac{E_{C^+} - E_x}{kT}\right) \exp\left(\frac{-4\pi}{h} \int_0^{X_E} [2m_n^*(E_C - E_x)]^{0.5} dx\right) dE_x \quad 2.38$$

where E_x is the energy component in the X direction and $E_{min} = \max[E_x(0-), E_C(W)]$ as visualized in Fig. 2.3 [YEH93; Sil16]. If tunneling current transport across the heterointerface is neglected, δ becomes zero.

The band edge is approximated as a linear function of position in the wide-band gap materials. The slope corresponds to the electric field at the interface. Therefore, the tunneling current based on δ in Eqs. 2.36 and 2.37 is based on the value of the electric field at the interface, thus the injected current occurs entirely at the interface. Accuracy limitations may arise for cases where non-local effects cannot be accounted by this approach. Indeed, tunneling is possible over a range of energies and a more accurate approach is to consider the non-linear shape of the potential barrier shown in Fig. 2.3. If the process is elastic, it can be approximated — in a very similar way as tunnel junction devices described in section 2.8 — by a carrier generation or recombination term throughout the depletion region (see for instance section 6.2.3 in [Sil16]). Although accuracy is increased, this typically involves an additional mesh region to deal with it.

Figure 2.3: Example of band profile of an abrupt heterojunction. Diagram adapted from [YEH93].

One of the advantages of thermionic models is that they are able to include mechanisms that dominate the current transport in a heterojunction (TE and TFE). In the diffusion model, the quasi-Fermi level is continuous across the interface, thus the current transport at the interface is not considered explicitly. A key factor of thermionic models is that exactly at the heterojunction, an additional node mesh is placed at the interface between low and high bandgap materials where two distinct properties coexist.

The additional node mesh where Eqs. 2.36 and 2.37 are solved instead of drift-diffusion equations is set at all heterojunctions that appear in a multijunction solar cell structure (i.e., window/emitter, base/BSF interfaces...).

2.7 Drift-Diffusion with position dependent band structure

So far, the set of equations described previously enables the calculation of homojunction structure domains (same material). Multijunction solar cells made up of several semiconductor materials with distinct properties (i.e., bandgap, electron affinity, effective mass...). Therefore, the transport equations should be modified according to the position-dependent band structure [LS82; LS83]. The conduction and valence band energies are written including the position-dependent electron affinity (χ) and some reference potential (ψ_0)⁶:

$$E_C = q(\psi_0 - \psi) - \chi, \quad 2.39$$

⁶See [Lun06] for an excellent guide on how to build energy band diagrams for heterostructures.

$$E_V = q(\psi_0 - \psi) - \chi - E_g \quad 2.40$$

Then, ψ_0 is also defined by:

$$\psi_0 = \frac{\chi_r}{q} + \frac{kT}{q} \ln \frac{N_{cr}}{n_{ir}} = \frac{\chi_r + E_g}{q} - \frac{kT}{q} \ln \frac{N_{vr}}{n_{ir}} \quad 2.41$$

n_{ir} is the intrinsic carrier concentration of the arbitrarily reference material and r is the index that indicates all of the parameters are taken from reference material. Fermi energies are now expressed as:

$$E_{FN} = E_C + kT \ln \frac{n}{N_C} - kT \ln \gamma_n \quad 2.42$$

$$E_{FP} = E_V + kT \ln \frac{p}{N_V} + kT \ln \gamma_p \quad 2.43$$

If one assumes Boltzmann statistics, $\gamma_n = \gamma_p = 1$ which means that the last term in Eqs. 2.42 and 2.43 are related to the Fermi-Dirac statistics. These terms are then:

$$\gamma_n = \frac{\mathcal{F}_{1/2}(\eta_n)}{e^{\eta_n}}, \quad 2.44$$

$$\gamma_p = \frac{\mathcal{F}_{1/2}(\eta_p)}{e^{\eta_p}}, \quad 2.45$$

where

$$\eta_n = \frac{E_{FN} - E_C}{kT} = \frac{1}{\mathcal{F}_{1/2}} \frac{n}{N_C}, \eta_p = \frac{E_V - E_{FP}}{kT} = \frac{1}{\mathcal{F}_{1/2}} \frac{p}{N_V} \quad 2.46$$

Finally, drift-diffusion equations for position dependent band structure are defined by combining the current density expressions $\vec{J}_n = -q\mu_n n \nabla \phi_n$ and $\vec{J}_p = -q\mu_p p \nabla \phi_p$ with $\phi_n = -\frac{1}{q} E_{FN}$ and $\phi_p = -\frac{1}{q} E_{FP}$:

$$\vec{J}_n = kT\mu_n \nabla n - q\mu_n n \nabla \left(\psi + \frac{kT}{q} \ln \gamma_n + \frac{\chi}{q} + \frac{kT}{q} \ln N_C \right), \quad 2.47$$

$$\vec{J}_p = -kT\mu_p \nabla p - q\mu_p p \nabla \left(\psi - \frac{kT}{q} \ln \gamma_p + \frac{\chi + E_g}{q} - \frac{kT}{q} \ln N_V \right) \quad 2.48$$

2.8 Non-local band to band tunneling models

Historically band to band tunneling (BBT) models have been used extensively to describe the tunneling effect in many devices. They do not require numerical integrations either the search of critical points (or turning points), thus they are practical and efficient. Nevertheless, they calculate the recombination-generation rate at each point based on the electric field value at that

local point. As the pn junction becomes narrower, the local models and drift-diffusion approach start to fail. Additionally, the trap assisted tunneling (TAT) effect is required to explain the excess current in the valley region of tunnel junctions. In fact, Baudrit & Algorta revealed the importance of using non-local models and real doping profiles to fully describe experimental I-V curves [BA10].

According to this, what BBT and TAT miss, in general, is the spatial variation of the energy bands, thus the whole electric field profile influence on carriers. It is also obviated the fact that generation-recombination of opposite carrier types is not spatially coincident. A schematics illustrating the differences between non-locality for TAT (NLTAT) and the BBT (NLBBT) is illustrated in Fig. 2.4

Figure 2.4: Energy band diagram schematic illustrating the TAT, NLTAT and NLBBT for a highly doped p-n junction.

We follow the non-local models which are an extension of Hurx's model [HKK92]. These models are already included into the simulator and were corroborated in a GaAs/GaAs tunnel junction by Baudrit & Algorta [BA10]. Here we provide a very brief overview while more details on the modelling can be found in [Sil16].

Non-local models are only suitable for pn junctions, not unipolar devices and they require an additional mesh. Since the quantities between meshes (tunneling and background) are interpolated, it is critical to define a fine mesh with similar spacing in tunneling regions. Tunnelling mesh can be defined by quadrilateral regions that may or may not be uniform [Sil16]. This is indeed required for the simulation of multijunction devices in 2D where non-uniformities in the background mesh along the x-direction are present (as shown in Fig. 2.2).

The tunneling current for an electron is calculated as[Sil16]:

$$J(E) = \frac{qkT\sqrt{m_e m_h}}{2\pi\hbar} T(E) \times \left[\log \left(\frac{(1 + \exp[E_{Fr} - E]/kT)(1 + \exp[E_{Fl} - E - E_{max}]/kT)}{(1 + \exp[E_{Fl} - E]/kT)(1 + \exp[E_{Fr} - E - E_{max}]/kT)} \right) \Delta E \right] \quad (2.49)$$

where $T(E)$ is the tunneling probability, E_{max} is the energy value lower than the highest energy where tunneling is possible, E_{Fr} and E_{Fl} are the Fermi levels of majority carriers at the right and left side of the junction and the other variables have their usual meaning. The models for trap assisted tunneling (local or non-local) are implemented via carrier lifetime enhancement factor inserted into a SRH equation. The enhancement factor for non-local models and electrons is defined by:

$$\Gamma_n^{DIRAC} = \frac{1}{kT} \int_0^{\Delta E_n} e^{E/kT} T_{trap}(E) dE \quad 2.50$$

where $T_{trap}(E)$ is the probability that an electron with energy E tunnels elastically to the conduction band from the trap position and it is calculated by WKB method. ΔE_n is tunneling energy range for electrons. The exponential term gives the probability that the electron will gain energy ($\Delta E_n - E$) from phonon interactions before tunneling. Similar expressions are defined for holes. Then the effective carrier lifetime inserted into the SRH equation is:

$$\tau_{n,p,eff} = \frac{\tau_{n,p}}{1 + \Gamma_{n,p}^{DIRAC}} \quad 2.51$$

2.9 General boundary conditions

Several boundary conditions could be defined along and through the structure. We refer to general boundary conditions to those that are intended to apply current/voltage biasing with specific models to be solved. Accordingly, this kind of boundary condition will be referred to as an electrode region with zero thickness.

2.9.1 Ohmic contacts

Dirichlet boundary conditions are used to emulate ohmic contacts. The potential, electron and hole concentrations (ψ_s, n_s, p_s) are fixed at the surface. Minority and majority carrier quasi-Fermi potentials (ϕ) are assumed to be equal to the applied bias on the electrode. Consistent with space charge neutrality, ψ_s is given by:

$$\psi_s = \phi_n + \frac{kT}{q} \ln \frac{n_s}{n_{ie}} = \phi_p - \frac{kT}{q} \ln \frac{p_s}{n_{ie}} \quad 2.52$$

where

$$n_s + N_A^- = p_s + N_D^+ \quad 2.53$$

The quasi-Fermi potentials are known, thus eq. 2.53 can be solved for ψ_s, n_s and p_s . If Boltzmann statistics is used, these quantities are calculated as follows [Sil16]:

$$n_s = \frac{1}{2} \left[N_D^+ - N_A^- \sqrt{(N_D^+ - N_A^-)^2 + 4n_{ie}^2} \right], \quad 2.54$$

$$p_s = \frac{n_{ie}^2}{n_s}, \quad 2.55$$

2.9.2 Distributed specific contact resistance

Current transport along the metal/semiconductor interface can be accounted for by the boundary physics described in previous sections, either by assuming an ideal contact or a Schottky contact. Typical metal/semiconductor contacts in solar cells behave as an ohmic contact with finite resistivity and non-uniformities in the electrostatic potential that can be accounted for by a distributed contact resistance. Usually, the distributed contact resistance ranges between 10^{-4} and $10^{-6} \Omega \cdot \text{cm}^2$. In order to account for the finite resistivity and non-uniformities along the contact (either ohmic or Schottky), an effective value of resistance is assigned to the element associated to the contact and dependent on the length of that element. Accordingly, for steady-state conditions the following equation must be satisfied [Sil16]:

$$\frac{1}{R_i} \left[V - \left(\psi_i \pm \frac{kT}{q} \ln(N/n_i) \right) \right] - (I_n + I_p) = 0 \quad 2.56$$

where V is the voltage applied to the contact, ψ_i the surface potential, N is the net doping, I_n, I_p the electron and hole currents at node i and R_i the effective resistance value calculated as:

$$R_i = \frac{R_{con}}{d_i \cdot width} \quad 2.57$$

d_i is the length associated to the element, $width$ corresponds to the width of the device and R_{con} is the input parameter that can be associated to the conventional parameter used for specific contact resistance widely used in circuit simulators.

2.9.3 Neumann boundaries

Homogeneous Neumann boundary conditions are set on the outer boundary domain, at the edges of devices. This means that the current only flows out of the device through the contacts. In the absence of surface charge along such edges, the normal electric field component becomes zero. Current is not allowed to flow from the semiconductor into an insulating region (except via oxide tunneling models). At the interface between two different materials, the difference between the normal components of the respective electric displacements must be equal to any surface charge according to:

$$\hat{n} \cdot \varepsilon_1 \Delta\psi_1 - \hat{n} \cdot \varepsilon_2 \Delta\psi_2 = \rho_s \quad 2.58$$

where $\hat{n}$ is the unit normal vector, ε_1 and ε_2 are the permittivities of the materials on either side of the interface and ρ_s is the sheet charge density at the interface.

2.10 Conductors and insulators

TCAD simulators usually classify materials into three categories: 1) semiconductors, 2) conductors and 3) insulators. The semiconductor equations have been already described. Current flow at the conductors is handled by the Ohm's law:

$$J = E/\rho \quad 2.59$$

where E is the electric field, ρ the resistivity of the material and J the current density. In addition, thermal coefficient parameters should be specified. These regions are called conductors rather than metals because it is possible to define metals and semiconductors as conductive regions. The modelling of any region by using Eq. 2.59 is useful for simulations that consider resistivity losses, e.g., the front metal grid. It is appropriate to remind that currents and potentials can only be applied/extracted directly by electrodes and not from metal regions, thus it is still required to define electrodes on the desired part of a metal region (i.e., the top surface of the metal grid). If the metal resistivity is considered, one may think that a distributed contact resistance acting on an electrode and semiconductor interface could be missed. In our case, an interface contact resistance between a conductor and a semiconductor region can still be simulated in a similar way as explained in section 2.9.2.

For insulators, only the Poisson and lattice heat equations are solved. No mobile charges ($n = p = C = 0$) are assumed and electrostatic potential follows Laplace equation:

$$\text{div} \nabla \psi = 0 \quad 2.60$$

2.11 Summary of models and general assumptions

According to the description of the above subsections, the models and assumptions made in the simulation framework for solar cells in this thesis are:

- Drift-Diffusion models assuming parabolic band structure.
- Isothermal simulations (spatially uniform temperature).
- Electron and hole temperature equal to lattice temperature (no heat flux equation solved).
- Carrier transport via drift and diffusion for material bulk and homojunction interfaces.
- Thermionic and thermionic field emission current transport for abrupt heterojunctions
- Non-local band to band models for tunnel junctions as well as local and non-local trap-assisted tunneling consideration.
- Piezoelectric and magnetic fields are not considered.
- Isotropic refractive index for any material.
- Uniform and isotropic minority carrier properties for each region (i.e., μ and τ), mainly dependent on the doping concentration and material, unless specified.
- Normal incidence of light.

2.12 Limitations

The TCAD framework used here has some limitations that must be discussed to provide a grounded basis or whether or not to be confident with the outputs of the simulator. This simulator is very useful for the analysis of the devices, providing insight into the main losses within the structure and to test new structures. However, it must not be forgotten the strong dependence on the input parameters provided and the models used. Many of those parameters are very difficult to measure, the methods may have a high degree of uncertainty and they can be very time consuming. The lack of important parameters such as trap characteristics, minority carrier lifetime variations (i.e., its dependence with injection level) are some examples of the complexity in gathering reliable parameters.

Besides the limitations that can be deduced from the general assumptions listed previously, we describe below what we consider the main specific limitations in the multijunction device modelling developed in this work.

- **Photon recycling (PR)**

Photon recycling is not considered self-consistently. Rather, it is taken into account via an effective radiative recombination coefficient. Let us consider an isotropic radiative recombination coefficient that can be calculated by the following expression [WCW15]:

$$B = \frac{1}{n_i^2} \frac{2\pi}{h^3 c^2} \int_0^\infty \frac{n(E) \alpha(E) E^2}{e^{E/kT} - 1} dE \quad 2.61$$

For instance, for GaAs the calculated $B = 4.45 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. However, as we will see in Sections 3.2 and 3.3 and the Appendix, most of our data fitting required the use of lower values of B (in the range of $1 - 2 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) which implies that a significant amount of photon recycling is present, being around half of the calculated value via eq. 2.61. Although an effective value of B can accurately reproduce our experimental data, the self-consistent treatment of photon recycling is key to achieve high-degree of prediction capabilities for III-V materials, mainly because it will be dependent on injection level, doping concentration and thickness of the material. This will be of high importance if one performs optimizations of the structure (e.g. doping concentration). The use of an effective B coefficient may be only valid for a very restricted range of bulk thickness and doping concentrations. In fact, Martí et al. showed that the recombination pre-factor, I_0 (or the so called reverse saturation current) increases with thickness if photon recycling is not considered. When PR is taken into account, I_0 starts to saturate at a certain thickness depending on the material quality and the degree of PR exploitation (i.e., structure with back reflector, on-substrate, without substrate...) [MBR97].

The PR consideration is more important for cases where radiative recombination is dominant and photon recycling plays an important role. Therefore, in order to optimize the solar cell thickness, improved predictions will be attained by the consideration of PR. On the other hand, more rigorous approaches including self-consistent treatment of photon recycling within TCAD environments have been recently reported [Wal+15]. It has been shown that the differences with most of the thickness values used in this work (1-3.5 μm) ranges between 15-25 mV of V_{oc} difference (at 1-sun) depending on the material quality. This V_{oc} difference in the thickness-dependence has been calculated for materials without a substrate and including a very efficient back reflector ($R > 90\%$). All the structures

analysed in this thesis are on-substrate solar cells and strongly affected by perimeter recombination, thus the impact of PR on the V_{oc} is expected to be less than the maximum value of 25mV. Indeed, by using an effective B , the V_{oc} difference for devices with 1 or 3.5 μm is about 22mV in our calculations.

Accordingly, PR consideration is a must in III-V materials; however, the deviations by using an effective B coefficient may not be large in most of the cases analyzed in this work. For the particular case of multijunction devices (i.e., GaInP/GaInAs/Ge) its relative impact would be also lessened. All in all, as previously mentioned, the inclusion of photon recycling into TCAD environments has been demonstrated in the past years [PBS97; Bal04; LHB06; Wal+15; Ren+15] and this is one of the most important pending tasks of this work. It will acquire higher importance mainly because the inverted metamorphic (IMM) approach is being also developed in our laboratory with high material quality and including BSR. Moreover, it would be interesting to test new structures that increase the optical confinement.

• Luminescent Coupling (LC)

Luminescent coupling is closely related to PR because they both increase their importance as material quality and optical confinement is increased. The LC has been shown to be an important effect that influences the optimum design of a solar cell. This is essentially true for very high quality materials such as the ones demonstrated by IMM solar cells (see for instance [Gei+15b]). This effect is not included into our simulator. In this thesis, we have analysed by TCAD simulations conventional 3J solar cells on germanium, as well as 4J solar cells including dilute nitride materials. In both cases, the only cell with material quality that exhibits evidence of significant LC strength is the Ga(In)As subcell. Although present, the LC detected is far lower than the state-of-the-art ones demonstrated in the literature. Moreover in the case of the 3J cell, the additional photocurrent generated would be re-absorbed by the germanium subcell which typically exceeds by more than 20% the limiting photocurrent in the stack. In the case of the 4J, its performance is far to be comparable to a 3J case mainly because of dilute nitride limitations. Accordingly, the LC impact on both structures is expected to be rather low.

In any case, both, PR and LC are very important effects for very high quality materials, i.e., such as those exhibited by record III-V solar cells. Its influence increases for devices operating closer to the Shockley-Queessier (S-Q) limit and for those where new structural

designs are used to exploit the optical confinement [MYK12]. Although it may be computationally expensive (even more in multijunction cases), the self-consistent treatment of LC and PR into our TCAD environment is a must for very high quality materials in order to increase both *predictive* capabilities of the modelling and the reliability in the test of new structures. In the case of on-substrate solar cells such as the ones used in this thesis, its influence is lessened, but it is still an important effect to consider and it is still unanswered into what extent the effective radiative coefficient is good enough in these cases.

Accordingly, the inclusion of PR and LC are pending tasks intended to be covered in the future.

- **Dilute nitride simulation**

The modelling approach used has been based on parabolic bands and it is well-known that the dilute nitride band structure is non-parabolic. The impact of the inclusion of non-parabolicity into the drift-diffusion models is still yet to be determined for dilute nitride materials. Accordingly, the interpretation of the results in dilute nitrides modelling must be done cautiously.

2.13 Particularities of the simulation framework

2.13.1 Dimensionality

The dimension of the simulation domain is typically defined as a trade-off between accuracy and computation time. Obviously 3D is preferable to describe real geometries, but the computation time rises significantly when using 3D simulations and it would increase accordingly to the mesh gridding and models used. Symmetry planes and periodicity can be used to reduce the number of nodes, however, real solar cell device length ranges from tenths of mm to some hundreds and in some cases they can be very large (i.e. 8x4 cm for space solar cells) which even though applying the maximum symmetry cut planes, the number of grid points can still be very large. Indeed, computation time scales with the number of nodes as N^α (where α ranges between 2 and 3). Accordingly, TCAD 3D simulations require high computation resources and may not be feasible to execute routinely. It is usually more viable to make the structures simpler and apply certain assumptions that can still provide adequately accurate results. Fortunately,

solar cells are highly symmetric and most of the important phenomena can be considered. In this sense, most of the simulations performed here are 2D and in some cases (for geometry comparisons) 3D simulations were also performed. In many cases, it is also viable to perform one dimension simulations that provide valuable information in a fast manner while being aware of the specified limitations, i.e. no lateral current flow (or lateral conductivity), neither grid and busbar influence, nor perimeter recombination. Table 2.2 lists some of the limitations and advantages of different structures used as shown in Fig. 2.5 for the simulation of multijunction solar cells.

Figure 2.5: Dimensionality of the solar cell structures used in this thesis. The 3D structure corresponds to a quarter of an entire solar cell with and square-inverted grid design.

When the 3D structure is used for light I-V simulations (i.e. GaAs single junction), a 1D profile of the photogeneration rate $PGR(y)$ is calculated and mapped laterally (through the z-axis) onto the entire standard domain shown in Fig. 2.5 of the device simulation. PGR beneath metal fingers is assumed to be zero. Accordingly, the light incidence is considered to be normal and uniform in lateral dimensions. The reason to do this is because there is no implementation of fast and reliable methods such as the TMM in 3D in the simulator used. Ray-tracing can be used instead of TMM because of its 3D implementation, however, as mentioned previously ray-tracing lacks of important effects such as coherence. Besides, it is very time consuming because of a high number of rays must be defined to cover the whole geometry which significantly increases the computation time, e.g., $\sim 200 \times 200$ rays are defined in x and z-axis in order to properly illuminate and cover a surface region of $500 \times 500 \mu\text{m}$. It will take

Table 2.2: Main features of different dimensions for multijunction solar cell simulation (based on a 4J solar cell). ARC stands for anti-reflection coating.

Feature	1D	2D	3D
Current flow	Vertical	Lateral	Full geometry consideration ^a
S_f & S_b	$\rightarrow \infty^b$	Variable	Variable
ARC	Yes	Yes	Yes
Illumination	Uniform	Non-uniform ^c	Non-uniform
TMM	Yes	Yes	No ^d
Perimeter recombination	No	Yes	Yes
Tunnel junction	Yes	Yes	No
Metal grid	No	Partial metal grid/dark diode ^e	Full metal grid
Grid points ^f	< 2k	< 10k	> 200k

^a In the case of Fig. 2.5 this is essentially true when assuming maximum symmetry cut planes.

^b If ohmic contacts are used.

^c Typical illumination profile (i.e., Gaussian) under a concentrator requires a full 3D consideration (see [Gar10]).

^d If normal incidence is assumed, 1D TMM output results can be included into a 3D structure. See text.

^e See. section 2.13.3.1.

^f Excluding tunneling mesh.

take about 12 hours of computation time⁷ just to illuminate the structure.

2.13.2 Numerical precision

Another important fact regarding a convergent and accurate simulation of multijunction solar cells is that related to numerical precision. Materials with high bandgaps are frequently found in III-V multijunction structures. In some cases a high quality and high-bandgap material produces a very low saturation current that could be difficult to handle with just 64-bit usual arithmetic precision. Additionally, very low intrinsic carrier concentrations may be found in low-temperature simulations. In these cases, higher numerical precision is required. Therefore, the required precision (P) depends strongly on the bandgap and lattice temperature and can be estimated as [Sil16]:

⁷By using 8 processor unit at 3 Ghz.

$$P \geq \frac{1}{\ln(2)} \left(\frac{E_g}{kT} \right) \quad 2.62$$

It should be mentioned that inequality 2.62 provides just an estimation of the number of bits required. Nevertheless, it is possible to perform successful simulations with lower precision than required. For all multijunction solar cells simulated in this thesis 160-bits are good enough to obtain useful, accurate and convergent solutions. In the case of single junctions, higher arithmetic precision is not usually required.

2.13.3 2D simulation assumptions for experimental data fitting

2.13.3.1 Dark diode

Dark diode is usually referred to all region of the solar cell that are shaded by the front metal-lization grid (i.e. bus bars and grid fingers). Dark diode dimensions are dependent on the metal grid pattern used which varies substantially among solar cell manufacturers (either a company or a laboratory). In 2D simulations, it is not possible to include the real geometry of the device (e.g. grid pattern). To take into account real geometries, a full 3D approximation is required [Gal+05; GAR06; BA07]. For instance, 3D simulations would be of greater importance when inhomogeneities and non-uniformities (either in semiconductors structure, metal grid or light illumination) are considered. Nevertheless, regarding the influence of the dark diode, some simple approximations allow to take into account its effects, at least to some extent. The dark diode can be understood as an additional recombination area which results into an open circuit voltage reduction. Indeed, if we assume uniform properties and light illumination (as most of the cases analyzed in this thesis) the most affected parameter by the dark diode is the open circuit voltage. As a good approximation, the V_{oc} loss due to the dark diode can be roughly estimated by a modified expression from [Gei+15b]:

$$\Delta V_{OC} = \frac{mkT}{q} \ln \left(\frac{A_{illum}}{A_{total}} \right) \quad 2.63$$

where m is the number of junctions, A_{total} is the total area including the busbar while A_{illum} is the area not covered by metal. Although Eq. 2.63 is less accurate (independent of the biasing conditions) than other approaches (i.e., 3D circuit simulators), it provides an area dependence of the dark diode which can be directly included into the 2D simulations where operating biasing conditions are taken into account. For instance, let us consider a square solar cell (as frequently used within this thesis) with a front metal grid pattern whose active area is A_{illum} and a total area

A_{total} . To consider the full dark region area we equate the ratio A_{illum}/A_{total} to L_{illum}/L_{total} from Fig. 2.5.

The effects of the dark region are very important for comparison to experimental data. Indeed, for this type of metal grid, the V_{oc} loss (ΔV_{OC}) is on the order of 10 mV per junction according to Eq. 2.63 and could be higher for devices with ideality factors > 1 . For a 3J solar cell, about 30 mV loss can be due to the dark region and if neglected in the data fitting procedure, it could mislead the material quality of each junction.

The influence of the dark diode following the simple assumptions made here were compared to results obtained by using a quasi-3D circuit simulator [Gal+05]. Perimeter recombination is not included and to make the comparison more valid, the metal grid resistance is also neglected. Distributed front contact resistance ($10^{-6}\Omega\cdot\text{cm}^2$) is included in both TCAD and quasi-3D circuit simulator. Comparable material properties (i.e. minority carrier properties to saturation currents, layer sheet resistances, etc.) were set, thus their dark I-V curves are similar. We use as a figure of merit for the comparison the V_{oc} loss due to dark region (ΔV_{OC}). Therefore, ΔV_{OC} is calculated for a set of 3J solar cells with bus length (or L_{dark} from Fig. 2.5 in 2D-TCAD cases) variations covering dark areas from 10% to 100% with respect to the illuminated area for different light concentrations. This means that 100% dark area is for a case where the illuminated area is half of the dark one. The ΔV_{OC} is obtained by making the difference between the case with some shadowing and one without it (by artificially including transparent electrodes).

As can be seen in Fig. 2.6, ΔV_{OC} calculated following 2D-TCAD simulations are systematically higher than quasi-3D circuit ones for any dark area considered. The curves are almost constant up to 300 suns. Above this concentration, ΔV_{OC} starts to increase due to series resistance (contact resistance and/or top semiconductor layers) which is captured similarly by both approaches. Maximum deviations between simulations are lower than 14 mV in the extreme case, i.e., 100% dark area. Such deviations seem affordable when using simple structures (2D-TCAD). Indeed, most of the simulations performed here were compared to structures that have about 44% of dark areas where a maximum deviation of 7 mV could be expected by using one or another approach. Interestingly, although the voltage loss calculated with Eq. 2.63 is constant with light concentration as shown in Fig. 2.6 and does not follow the trend of 2D-TCAD and circuit simulators (which are more realistic approaches), the deviations are still reasonable even at high concentrations.

Dark areas in commercial CPV solar cells are up to 10% of the total area (see for instance [Spe]). The total V_{oc} loss in this case gets substantially diminished down to a point that the difference between approaches is almost negligible ($< 1\text{mV}$) for any concentration. Accordingly,

Figure 2.6: V_{oc} loss due to dark areas in a 3J structure and estimated with three different approaches, namely: 2D-TCAD, quasi-3D circuit simulator and Eq. 2.63. Percentage numbers indicate the dark area with respect to the illuminated one. Symbols indicate calculated values and lines are a guide to the eye.

for typical metal grid losses found in commercial devices, the V_{oc} difference due to dark diode (without considering perimeter recombination) between quasi-3D circuit simulations and 2D-TCAD can be assumed to be negligible.

2.13.3.2 Series resistance

The front and back contact resistances were calculated by implementing a distributed contact resistance which takes into account possible non-uniformities in the electrostatic potential along the metal-semiconductor contact, see section 2.9. The device simulator is not suitable for dealing with the 3D metal grid losses due to the large number of nodes required to properly define the device geometry and the high computational resources required to solve the basic semiconductor equations and extra models. This is one of the reasons why the third dimension (z) is omitted in most of the simulations presented in this thesis. Another reason is the fact that the tunnel junction modelling has not been implemented in 3-D. Consequently, the metal grid losses were calculated after each simulation by using a lumped model following the approach explained in [AD00].

2.13.3.3 Temperature

Simulations are typically performed at 300K and laboratory measurements at 298K. This two-degree difference could have an impact on several temperature-dependent fundamental material properties. Perhaps the most important ones involve those of the bandgap and dielectric per-

mittivity as well as the carrier mobilities and lifetimes, just to name a few. In the case of I-V parameters, the J_{sc} changes can be captured explicitly through QE measurements and modification of the absorption coefficient and they are lower than the open circuit voltage dependency. Indeed, this is highlighted in multijunction solar cells where more than one material and pn junction are stacked. Typically in multijunctions, a 3J device drops about 7-10 mV/K [SB14] and a bit lower (about -2.5mV/K) in a 2J case including luminescent coupling at 1-sun operation [Och+16b]. Therefore, non-negligible deviations could be found as the number of junction increases. Accordingly, all simulations performed (unless specified) were set at 298K.

2.13.4 Data fitting procedure

Input parameters are critical to obtain reliable and physically meaningful simulations. In drift-diffusion simulators one must include a set of material parameters and models as input data. In some cases, those material parameters are well-known, but in many cases high complexity in their estimation and time-consuming and intricate experiments are required. It is usually most feasible to extract them by inverse modelling. Here we describe the general methodology followed to increase the confidence and reliability in data fitting performed in all comparisons with experimental data. To achieve a successful validation, the structural properties as well as the electrical and optical properties and parameters must be known. Prior to extract the electro-optical properties of a given structure, one has to depart from well-known structural properties, whose measurement is recommended, at least for the the most critical parameters, i.e., doping concentrations. Then, the material parameters and model validation starts from a solid basis. To illustrate the importance of material parameters, let us consider an example. The external quantum efficiency curve is commonly fitted to extract the diffusion length of carriers. If the optical behavior of the solar cell structure is not accurately validated by using proper models and optical constants, the estimation of the carrier diffusion length will be misleading. To provide a higher degree of confidence, we compare the simulation results to a wide set of typical PV characterization such as QE, R, light and dark I-V curves. Accordingly, reflectance fitting serves as a feedback for the evaluation of the optical constants and thickness of the layers, while the QE involves the absorption of the structure as well as the carrier diffusion length. The diffusion length is further validated by a proper data fitting to the dark and light I-V curve by varying lifetimes, mobilities, recombination coefficients, etc. In some cases, due to the high correlation between parameters and the unknown variables, we perform sensitivity analysis to determine the range of possible values able to achieve a suitable data fitting. Accordingly, albeit time-consuming, this multiple data fitting provides a higher degree of confidence in the material

parameters and models used. Fig. 2.7 shows the flow diagram we have followed in simulations used for validation of the model.

Figure 2.7: Flow chart we follow for the validation of material parameters and models.

2.13.5 Basic definitions for TCAD analysis

Most TCAD environments do not directly provide useful outputs for solar cell analysis. For example, it is not possible to directly extract the QE contributions by regions neither the subcell I-V curve of a multijunction structure. However, the simulator provides all useful quantities required for their calculation, i.e., recombination-generation values as a function of the position within the structure and operating bias (voltage, current or light). Here we detail how the QE, collection efficiency (CE) and subcell I-V curves have been extracted.

2.13.5.1 Quantum Efficiency (QE) and Collection Efficiency (CE)

The QE contribution of each layer is calculated by integrating the difference between generation and recombination rates along the semiconductor structure volume for every photon wavelength (λ) and normalized to the total photogeneration coming from the source [FF10]. Assuming uniform behavior along the length and width of the structure, the EQE by regions is defined by:

$$EQE_r(\lambda) = \frac{\text{carriers collected}}{\text{incident photons}} = \frac{q \int_{y_1}^{y_2} G(\lambda, y) - \mathcal{R}(\lambda, y) dy}{I_s(\lambda)} \quad 2.64$$

where EQE_r is the EQE of any region r (e.g. absorber) defined within the structure between coordinate y_1 and y_2 , G is the rate of photons absorbed, $\mathcal{R}$ the total recombination and I_s is the source monochromatic beam converted into electrical current. I_s is an output quantity provided by the simulator [Sil16].

The total EQE of the device is the sum of all region contributions. Notice that if recombination exceeds generation in some regions would result in some sort of *negative* quantum efficiency according to the EQE definition of Eq. 2.64. This unbalance means that electrons generated at one region are recombined in a different region. For instance, this could happen in an absorber whose we want to separate the contribution from the space charge region (assuming negligible influence of the monochromatic beam on the depletion width) and the quasi-neutral regions. If electrons generated at the space charge region are able to reach the quasi-neutral region and recombine there rather than travelling to the other side of the pn junction to be collected, *negative* QE rises. This may occur for cases where the absorber minority carrier properties are significantly poor. QE is inherently positive by definition, but internal processes may change the generation-recombination difference. In such cases it would be indicated through the text that the *negative* QE is set to zero (unless specified) and the recombination *excess* is added to one of the adjacent regions in order to be consistent with the total QE of the device. Looking at *negative* QE is a powerful way to evaluate a region with very high recombination.

The CE is simply the ratio between carriers extracted to the carriers generated:

$$CE_r(\lambda) = \frac{\text{carriers collected}}{\text{carriers generated}} = \frac{q \int_{y_1}^{y_2} G(\lambda, y) - \mathcal{R}(\lambda, y) dy}{I_a(\lambda)} \quad 2.65$$

where I_a is the rate of photons absorbed by the structure converted into electrical current. In other words is the normalized maximum photocurrent that can be extracted from the structure considering no reflection losses and the absorption of the structure. I_a is an output quantity given by the simulator [Sil16].

For multijunction purposes, the experimentalist typically measures the subcell QE of a multijunction structure by sweeping a monochromatic light beam in the range of the subcell of interest while saturating the rest of the subcells with additional light sources (i.e. LED light) and setting appropriate voltage bias to ensure: 1) that the rest of the subcells do not limit the overall photocurrent; and 2) short circuit conditions on the subcell to be measured are achieved [Meu+03; Bar+15a]. This means that one has access to the subcell QE by using two terminals: anode and cathode. This could be exactly emulated by the simulator in order to calculate the desired subcell QE. A different strategy will be described in the next section.

2.13.5.2 I-V

The recombination current contribution by each region is simply calculated by integrating the recombination rate over the semiconductor region of interest multiplied by the electron charge at each voltage point, such as:

$$IV_r(V) = q \int_{y_1}^{y_2} \mathcal{R}(V, y) dy \quad 2.66$$

One could also assign $\mathcal{R}$ by any type of recombination (SRH, Auger, radiative...) either in QE or I-V analysis in order to separate the contribution of each type of recombination.

To extract the subcell characteristics (QE or I-V) there are different possibilities. One option is to extract the current-voltage pairs by calculating the current within a specific region (absorber, subcell...) by the convolution of EQE_r with the corresponding spectrum. The voltage could be extracted by looking at the quasi-Fermi level separation in a given region, or through [WW16]:

$$V = \frac{1}{q} \int_{left}^{right} \nabla \varepsilon_{FC}(y) dy \quad 2.67$$

where ε_{FC} is the Fermi energy of the conduction band. Using equation 2.67 requires a careful and appropriate definition of the left and right terminals to define the desired region within the structure where the voltage is extracted.

Extracting $\mathcal{R}$, G and other quantities as a function of the operating bias could significantly increase the simulation time. Thus, it is sometimes more practical to define *artificial* electrodes between subcells to calculate their QE or I-V. For instance, in a tandem device one can place electrodes — with ohmic boundary conditions— at the top surface (above the window layer) and at the back of the so-called back surface field layer (or at the anode/cathode boundary with the TJ to include its losses) in each subcell. Then, the subcell current-voltage characteristics are extracted straightforwardly from the additional electrodes.

CHAPTER 3

Simulation, characterization and analysis of GaAs, GaInP and Ge single junction solar cells and tunnel junctions

3.1 Introduction

This chapter deals with the simulation, characterization and analysis of different III-V single junction solar cells and tunnel junctions capable of being components of multijunction solar cells. Specifically, we analyse individually the ones intended to be used in a lattice matched GaInP/Ga(In)As/Ge 3J solar cell although they can be also incorporated in advanced 4J to 6J architectures. The analysis of particularities of each solar cell is presented. First, we examine GaAs single junction solar cell including a model for perimeter recombination to determine the impact of different sizes, doping concentrations and geometries. Perimeter recombination is only analysed in GaAs solar cells mainly because its impact on GaInP and Ge subcells has been shown to be rather low, even at high perimeter-to-area ratios [Esp+15b]. After that, the GaInP solar cell model is developed and a theoretical assessment of this solar cell for multijunction purposes is carried out. In particular, we evaluate the trade-off between V_{oc} increase due to larger bandgaps and thickness increase to preserve current matching conditions in a GaInP/Ga(In)As/Ge 3J solar cell. The germanium solar cell is studied in detail as well as the degradation of its electrical performance when subjected to different thermal loads (i.e. the growth of upper subcells). Finally, non-local tunnel junction models have been applied to a set of different structures such as AlGaAs/GaAs and AlGaAs/GaInP high-bandgap tunnel junctions in order to validate their performance prior their inclusion in a multijunction cell.

3.2 Analysis of GaAs solar cells

Most of the solar cells used within this subsection correspond to the millimeter-range size where perimeter recombination is an important issue [Ste+90b; Och+14]. Accordingly, the GaAs solar cell subsection is divided in two parts: 1) we first introduce a model of perimeter recombination validated to a set of different geometries, sizes and properties of fabricated GaAs diodes where 3D simulations have been used and 2) we present the analysis of the performance of such solar cells including perimeter recombination under different conditions.

3.2.1 Modelling perimeter recombination in a 3D TCAD environment

Atlas 3-D simulator is based on prismatic meshes and has been developed from 2-D codes that use triangular meshes. This means that the third dimension is created by stacking 2-D slices along the z-direction. Dealing with a 3-D problem involves a number of equations at least one order of magnitude greater than a 2-D problem [Cia+89]. For large problems as will be the case

shown in following sections (greater than 5000 grid points), iterative and direct solvers can be used. In this study, we have used iterative solvers due to the lower solution time and memory usage [Sil12a; Cia+89].

Additionally, one of the main issues in multi-dimensional device simulation is the mesh definition or gridding. Perimeter recombination is very dependent on the mesh resolution. In order to provide a high-degree of accuracy, the mesh spacing near the surface perimeter must be as low as possible, otherwise, the influence of perimeter recombination in the dark I-V curve will be overestimated for a particular set of interface parameters. In our simulations we have avoided this problem by setting the mesh spacing adjacent to the perimeter equal to 1 nm while the spacing increases progressively towards the bulk region.

3.2.1.1 Brief review on device modelling of perimeter recombination in GaAs solar cells

Perimeter recombination must be mitigated in order to increase the efficiency of III-V concentrator solar cells. Because of the complexity of the triple junction solar cells (GaInP/-GaInAs/Ge), it is recommendable to start analysing independently each subcell. So far, the most studied subcell has been the middle cell by analysing the GaAs single junction diode [Esp+10; Dod+91; MM93; BK06]. It must be taken into account that because of the negligible composition of indium (1.2%) of the GaInAs middle cell, the analysis of single junction GaAs cells grown on GaAs substrates is a valid approach in order to extract conclusions for the triple junction cells. In addition to the usefulness of understanding the GaAs cell perimeter recombination for multijunction solar cells, the recent proposal of using GaAs single junction solar cells for competitive cost of photovoltaic electricity [Atw11] adds interest to this study. It is well known that, as the perimeter-area ratio (P/A) increases, the perimeter current reaches significant values that can lead to a decrease in the open circuit voltage and to an important contribution to degradation mechanisms in GaAs solar cells [Esp+10]. Therefore, the performance of small size solar cells such as the ones used in concentration applications can be affected by perimeter recombination. For example, for modern GaAs solar cells, chemical treatments have been proposed [SEA12] in order to decrease the impact of perimeter recombination.

The dominant sources of perimeter recombination are surface states. Their main origin comes from dangling bonds at the surface and their formation is due to the loss of periodicity in the crystal (surface states are also created in between interfaces in the crystal and metal-semiconductor contacts but, in this section we will refer to surface states just at the perimeter of the whole structure). The formation of surface states is very dependent on the mesa-etching process, crystal orientation, surface oxidation, adsorption of impurities at the surface, among

others. The surface states energy levels can have a strong effect on the electrical characteristics of the semiconductor because the ionic charges on or outside the semiconductor surface induce image charges in the semiconductor causing the formation of the so-called surface channel or surface depletion-layer which is a region where minority carriers can be confined. Once this channel is formed it gives rise to a surface leakage current [Sze81].

Perimeter recombination in GaAs diodes, transistors and solar cells has been experimentally analysed and modeled by using 1-D and 2-D approaches by several authors [Esp+10; HLM78; TFW88; Dod+91; MM93; BK06]. The first approximation to describe this phenomenon was made by Henry et al. [HLM78]. They proposed an analytical expression (3.1) to obtain the perimeter current assuming: a) Fermi level pinning and b) constant electron and hole densities at the surface.

$$J_{per} = qS_0L_s n_i e^{\frac{qV}{2kT}} \quad 3.1$$

where S_0 is the called *intrinsic surface recombination velocity*, which is mainly determined by the density of surface states and their capture cross sections. L_s is the *surface diffusion length* and characterizes carrier injection and recombination in the surface channel. For Henry et al. the perimeter recombination is controlled by recombination in the *surface channel* (originated to preserve the surface charge neutrality) outside the region where the junction space charge layer intersects with the perimeter and has a $2kT$ -behaviour at low forward bias. Later the bias dependence of the ideality factor was studied by Tiwari et al. [TFW88] showing that perimeter recombination exhibits a $2kT$ -dependence close to the junction but a kT -dependence in the quasi-neutral regions. Dodd et. al. [Dod+91] calculated an effective width (where the perimeter recombination occurs) as a function of the electric field at the surface. Then, the perimeter recombination current was obtained by integrating the recombination rate (obtained numerically) all over the diode's perimeter [Dod+91]:

$$I_p = qP \int R_s(y) dy \approx qn_i S_0 L_s P (e^{q\frac{V}{n kT}} - 1) \quad 3.2$$

where P is the diode perimeter, L_s is the effective width for surface recombination, $S_0 = \sqrt{S_{n0} \cdot S_{p0}}$ the recombination velocity of carriers at the surface and n the ideality factor associated with the perimeter current. Dodd et. al. also showed that most of the recombination with $2kT$ behaviour took place at low biasing where the space-charge region intersected the perimeter. At higher biasing, the carriers injected in the quasi-neutral regions diffused toward the perimeter where they recombine. Under such conditions the perimeter current ideality factor decreases. Then, Mazhari et. al. made some corrections to the Henry model and got an analytical equation to describe the contribution of the quasi neutral regions to the perimeter

recombination. They stated that the kT -behaviour assumed at high forward bias is not always correct and depends on the surface recombination velocity, the doping level and the conductivity of the regions (n or p) [MM93]. Mazhari et. al. did not predict the current dependence on the doping level, just the nkT -behaviour.

Finally, Belghachi [BK06] et al. calculated separately the contribution to perimeter recombination current from the space charge region (analytical approach) and from the quasi neutral regions (numerical approach). For the contribution of the space charge region, they used the well-known expression for the perimeter recombination current (3.2) and they made an approximation to calculate the electric field. Regarding the perimeter recombination in the neutral region, they numerically solved the bi-dimensional steady state electron and hole continuity equations. In order to get the perimeter current they added the contribution from the space charge region and that of the quasi neutral regions.

In spite of all these studies, the perimeter recombination is still a phenomenon whose origins are not well known. Therefore, a general model with the following characteristics is required: a) absence of any restrictive assumption about external conditions such as current flows, voltage range, etc.; b) consideration of any kind of semiconductor structure: n/p or p/n, different doping levels and thicknesses of the layers, etc, c) 3-D (three dimensional) nature in order to evaluate real device characteristics such as geometry (circular, square, etc.), size, etc. Besides, a model with these characteristics would be able to show the real origins of perimeter recombination and would help to mitigate it.

3.2.1.2 Experimental

Two GaAs concentrator solar cell epiwafers, namely #A and #B were grown by MOVPE (Metal Organic Vapour Phase Epitaxy). Their structural characteristics are presented in table 3.1. The only nominal difference between them is the base doping level.

Front metallization was done by Au/Ge, Ni, Au evaporation while Au/Zn/Au were evaporated at the back contact. Both contacts were annealed in order to achieve ohmic contacts and they covered the whole surface of both sides in order to avoid crowding effects and to have a front metal close to an equipotential situation. After the ohmic contact formation, mesas were defined in order to isolate individual diodes. Circular and square GaAs diodes with different P/A ratios were manufactured as shown in figure 3.1 and table 3.2.

After diode manufacture, the dark I-V curves were measured using a conventional source-meter equipment. In order to measure the I-V curve of a diode, typically the source-meter is swept to a range of voltage and measure the resulting current. Four-wire technique was

Table 3.1: Structure of n/p GaAs diodes for the two #A and #B epiwafers.

Layer	Material	Thickness (μm)	Doping (cm^{-3})	
			#A	#B
CAP	GaAs:Te	0.17	$1 \cdot 10^{19}$	
	GaAs:Te	0.33	$1 \cdot 10^{18}$	
Window	$\text{Al}_{0.7}\text{Ga}_{0.3}\text{As:Si}$	0.04	$1 \cdot 10^{18}$	
Emitter	GaAs:Si	0.167	$1.5 \cdot 10^{18}$	
Base	GaAs:Zn	3.5	$3.5 \cdot 10^{17}$	$6 \cdot 10^{16}$
BSF	$\text{Al}_{0.35}\text{Ga}_{0.65}\text{As:C}$	152	$2 \cdot 10^{18}$	
Buffer	GaAs:Zn	1.16	$2 \cdot 10^{18}$	
Substrate	GaAs:Zn	350	$2 \cdot 10^{18}$	

Table 3.2: Geometrical characteristics of the square and circular diodes manufactured.

Perimeter (cm)		Area (cm^2)		P/A (cm^{-1})
Square	Circular	Square	Circular	Square and Circular
1.6	1.257	0.16	0.126	10
0.8	0.628	0.04	$3.14 \cdot 10^{-2}$	20
0.4	0.314	0.01	$7.85 \cdot 10^{-3}$	40
0.3	0.236	$5.63 \cdot 10^{-3}$	$4.42 \cdot 10^{-3}$	53.3
0.2	0.157	$2.5 \cdot 10^{-3}$	$1.96 \cdot 10^{-3}$	80
0.1	0.078	$6.25 \cdot 10^{-4}$	$4.91 \cdot 10^{-4}$	160

Figure 3.1: Picture of the resulting square and circular GaAs diodes with different P/A ratios on a 2-inch wafer portion. Courtesy of P. Espinet-González.

employed to avoid power loss due to wiring. The diodes were measured on a Peltier system to control their temperature in order to prevent voltage variations due to heating. The resulting dark I-V curves for several representative diodes of #A epiwafer are shown in figure 3.2 and they will be described later. The design of experiments was performed and led by P. Espinet-González. Here we only provide details on device manufacturing for clarification purposes in order to help the reading of the subsequent modelling which was performed by the author of this thesis.

Figure 3.2: Experimental dark I-V curves of square diodes for different (P/A) ratios of epiwafer A.

3.2.1.3 Modelling considerations

Regarding surface states, we use trap centres based on SRH recombination (similar approach as bulk) to calculate their contribution to the dark I-V curves. Although surface states could have multiple levels lying inside the forbidden bandgap, a single-level model is useful enough to describe their impact on the device behaviour. This can be implemented in two ways: 1) by reducing the carrier lifetimes by assigning an effective surface recombination velocity (SRV-model) and 2) by modifying the charge density at the surface by adding a specific density of traps (Trap-model). We have proved that both approaches are valid in order to model surface recombination in agreement with [Dod+91], but significant basic differences exist by using one or another. In fact, the presence of surface traps (Trap-model) creates an additional space charge region along the surface (neglected by the SRV-model) which alters the electrical interaction of carriers which can be important if the device is analysed under different external conditions. Therefore, the Trap-model describes more accurately the mechanisms by providing more insight to perimeter recombination and thus it is the model chosen in this thesis to analyse the origin of perimeter recombination in GaAs diodes and solar cells. The recombination terms are added to the carrier continuity equations in order to solve self-consistently the semiconductor fundamental equations to calculate dark I-V curves. The model employed is extensively described in sections 2.4.3 and 2.4.5.

3.2.1.4 Validation of the model

In order to validate the model, it has to be able to describe the experimental behaviour of perimeter recombination in GaAs diodes. This has been done by analysing how the model behaves while the constants or parameters are tweaked. The model has several adjustable input surface parameters: N_t , σ , E_t and g for both electrons and holes and for each type of trap (donor-like or acceptor-like) [ST71]. We have analysed the influence of each parameter in the dark I-V curve and verified by simulations that the impact of degeneracy factor and trap energy level (within a reasonable range) can be masked by a single defect level for these devices. Thus, all simulations were performed with a trap level located at the midgap in agreement with [Dod+91]. On the other hand, the densities of traps and capture cross sections have a strong influence on the I-V curve as figure 3.3 shows for N_t variations. As can be seen in figure 3.3 the perimeter recombination influence can be extended to high bias if N_t is high enough. Conversely, if the capture cross sections (not shown here) are increased it is also possible to obtain a high impact of perimeter recombination.

Figure 3.3: Influence of surface trap densities N_t located at midgap on the dark I-V curve for $P/A = 40$.

The model validation was carried out by fitting experimental dark I-V measurements such as those of figure 3.2 to the model. Accordingly, figures 3.4a and 3.4b show the fitting achieved for square and circular devices for #A epiwafer for three different P/A ratios while figure 3.4c shows the fitting achieved for square devices for #B epiwafer. It is remarkable that for both figures (3.4a and 3.4b) the only changed parameters for different diodes were their size and shape. While the rest of surface and bulk parameters were kept constant (see table 3.3).

Conversely, the only changed parameters for different diodes in figure 3.4 were their size and shape. Because #A and #B epiwafers have different doping levels, thus different bulk trap densities have been used for figures 3.4a/3.4b and 3.4c and their values are very similar to those found in [GOY90]. The surface trap parameters (similar to those found in [Dod93]) are the same for #A and #B epiwafers indicating that our mesa-etching process (same for both) is not sensitive to the base doping level analysed. The most reasonable values of trap parameters at surface and bulk were extracted by using a Levenberg-Marquardt algorithm [Sil12b] and they are listed in table 3.3. As a result, figure 3.4 shows that the model is able to simulate the whole I-V curves with high accuracy.

The measurements of the dark I-V curve show the influence of both the area and perimeter of the GaAs diodes. In order to better analyse the dark I-V curves (see figure 3.2) they were transformed into J_A -V curves (A/cm^2) by considering the diode area and J_p -V curves (A/cm) by considering the perimeter length in figures 3.5a and 3.5b, respectively. As can be seen, at low bias the current does not correlate with the area while it does with the perimeter so, the perimeter recombination dominates the dark current. At high bias, the results tend to show a mixture of area and perimeter correlation except for $P/A < 40$ which exhibits also a near perime-

Figure 3.4: Data fitting for: a) square devices and b) circular devices for #A epiwafer with $P/A = 160, 53, 40$ - in blue, red and green, respectively, and c) square devices for #B epiwafer with $P/A = 160, 40$ - in blue and green respectively. Lines are used for simulation and symbols for experimental data.

ter dependence. A similar behaviour was found for circular diodes. Manufactured diodes on #B epiwafer exhibit perimeter recombination extended to higher biases than #A epiwafer ones. Once we have proved the validity of the model and verified that dark I-V curves are affected by perimeter recombination, we are going to use the model to understand the origin and behaviour of perimeter recombination.

Table 3.3: Trap parameters at surface and in bulk used in simulations of diodes manufactured on #A and #B epiwafers.

Epiwafer	Type	N_t	Energy level	σ_n (cm ²)	σ_p cm ²)
#A, #B @Surface	Acceptor	$4 \cdot 10^{12}$ cm ⁻²	Midgap	$8 \cdot 10^{-15}$	$8 \cdot 10^{-15}$
	Donor	$4 \cdot 10^{12}$ cm ⁻²	Midgap	$8 \cdot 10^{-15}$	$8 \cdot 10^{-15}$
#A @Bulk	Acceptor	$6 \cdot 10^{13}$ cm ⁻³	Midgap	$1 \cdot 10^{-16}$	$1 \cdot 10^{-13}$
	Donor	$6 \cdot 10^{13}$ cm ⁻³	Midgap	$1 \cdot 10^{-13}$	$1 \cdot 10^{-16}$
#B @Bulk	Acceptor	$3 \cdot 10^{13}$ cm ⁻³	Midgap	$1 \cdot 10^{-16}$	$1 \cdot 10^{-13}$
	Donor	$3 \cdot 10^{13}$ cm ⁻³	Midgap	$1 \cdot 10^{-13}$	$1 \cdot 10^{-16}$

Figure 3.5: Dark a) $J_A - V$ curves and b) $J_p - V$ curves of square diodes for different (P/A) ratios of #A epiwafer.

3.2.1.5 Origin of perimeter recombination

Surface states at the perimeter of GaAs devices can be partially occupied by adsorbed atoms (such as oxygen, excess of arsenic, etc.) which set the character and ionization energy of the trap. Since we lack information about the energy level of the trap and the amount of charged

or neutral states at the perimeter, we have set equal trap density and energy level for electrons and holes. Therefore, surface states at the perimeter are able to trap electrons or holes with equal probability so, they can be neutral or charged depending on the position of the Fermi level. For p-type regions the position of the Fermi level lies closer to the valence band than the conduction band, which in fact sets the charge state (neutral or charged) of the traps. In such case, the acceptor-like traps (electron trap) are neutral and the donor-like (hole trap) are positively charged. In order to maintain charge neutrality the same amount of positive surface charge is screened with negative charges in the semiconductor bulk. This accumulation of charges makes the bands to bend downwards. The opposite behaviour applies to the n-type region, bending the band upwards. A representative picture of this can be found elsewhere [Mön01]. Accordingly, the band bending is characterized by a potential (reduced all along the perimeter with respect to bulk) that builds a surface channel where minority carriers are confined. Figure 3.6 shows the impact of the band bending in the electrostatic potential at equilibrium and the comparison between the built-in potential at surface (V_{bis}) and bulk (V_{bib}) of a diode of #A epiwafer. The interaction of carriers (mainly minority) with surface traps influences the distribution of the potential barrier V_{bis} at surface which is smaller (0.16V) than the built-in potential at bulk (1.39V) so, the potential barrier to be surpassed by carriers at the p-n junction will be lower at surface than in the bulk region (away from the surface).

Figure 3.6: Simulated 3-D plot of the electrostatic potential at equilibrium in P/A=160 diodes of the #A epiwafer. X coordinate shows a cross section of the diode where at 0 and 250 μm are placed at the borders of the structure where perimeter recombination appears. Y-direction (depth) at distances larger than 5 microns (substrate) is not shown for simplicity. The two dashed ellipses denotes the different potential barriers for carriers (see figure 3.7).

In addition, minority carriers from bulk also find a lower potential at the surface (0.56V from the base to the surface and 0.6V from the emitter to surface), away from the intersection of the p-n junction with the perimeter, than the one at bulk (V_{bib}). This potential corresponds to the difference between V_{bis} and V_{bib} (see figure 3.7).

Figure 3.7: Zoom of the dashed ellipses of figure 3.6 representing the cutline at perimeter ($V_{bis} = 0.16\text{V}$, green line) and bulk ($V_{bib} = 1.39\text{V}$, blue line) in the p-n junction. V_{bse} (0.6V) denotes the potential barrier seen by a carrier from the emitter bulk to the emitter surface (away from the depletion region where the potential is flat at bulk) if it moves in the same x coordinate. V_{bsb} (0.56V) is for case in the base region.

The surface channel region is associated to the local curvature of the bands which is proportional to the space charge density created by surface states. This curvature has two major characteristics such as its amplitude and width. The width (distance of the band bending from perimeter into the bulk) extends into the bulk until the band is flat. The wider the surface channel, the greater the space charge region from surface to bulk where minority carriers decrease. In the case of the amplitude of the band bending, the higher its value the easier for carriers to flow to that region. In figure 3.8 the potential distribution at the p-n junction is shown for three bias voltages. By increasing the forward bias, the voltage applied reduces the built-in potential at bulk and along the surface. Once the voltage bias reaches values above V_{bis} , the p-n junction at the surface is not longer a barrier but an electron sink. This causes the depletion region at the surface to begin to empty reducing the conduction surface channel width and amplitude by lowering its curvature so, the surface potential begins to be comparable to the one in bulk. Even at high bias, there is a lower potential at the perimeter. However, this happens in a very short distance and is no longer significant to the large amount of carriers at the bulk of the device.

The potential shown in figure 3.8 is related to the spatial distribution of charges affecting the carrier concentration, thus, the recombination rate. In figure 3.9 we can confirm the surface channel behaviour under forward bias by analysing the recombination rate at the same portion

Figure 3.8: 3-D plot of the potential at the p-n junction near the surface perimeter ($x=0 \mu\text{m}$) for #A (left) and #B (right) epiwafers under forward bias: a) 0.7V, b) 1V and c) 1.3V. The depth and width (along x coordinate) of the structure sides is shortened for simplicity. At the ground of the figures letter *E* denotes emitter while *B* is for base region.

of the device where the major influence of surface traps takes place. It can be deduced from figures 3.8 and 3.9 that minority carriers will recombine more at locations where they find the lowest barrier to overcome. The lower barriers are always found at the perimeter of the device but its contribution to recombination changes according to the bias applied. If we analyse the recombination rate under forward bias we can see that at any voltage the higher recombination is at the perimeter where the band bending and accumulation of charges is more pronounced. At low bias, there are locations at the perimeter junction and its surroundings with a high recombination rate coming mainly from the space charge regions. This recombination begins to spread

into the bulk as the bias voltage is increased. Therefore, at the vicinity of the space charge region at the surface and bulk the recombination rate begin to increase due to the fact that all traps inside the space charge region are ionized so, minority carriers begin to occupy bulk and surface trap states outside the space charge region. The latter makes the contribution of quasi-neutral regions significant as the voltage is increased. Hence, at higher biasing, the surface channel still acts as a sink of carriers but, the difference between bulk and perimeter recombination values is decreased. This reduction is enough to make the integration of recombination rate in bulk regions greater than the one at the surface.

The recombination rate is more extended into the base at bulk and perimeter on #B epiwafer than on the #A one due to the lower potential barrier found (see figure 3.8). This shows that perimeter recombination also depends on the doping level of the p and n regions. To the best of our knowledge this is the first time that the doping dependence of perimeter recombination is shown theoretically. Due to its importance, doping level is analysed in the next section.

3.2.1.6 Doping influence

In the work done by Mazhari et al. [MM93] the influence of doping level and dopant type was considered but only affecting the kT -recombination regime. Nevertheless, we will show below that the doping level could also affect the $2kT$ -recombination regime and plays an important role in the formation of the surface channel. In figure 3.10, two representative square diodes of the same size one manufactured on #A epiwafer and the other on #B epiwafer are compared. The diode manufactured on #B epiwafer exhibits higher recombination current. This is an interesting result that has not been explained in the past. The larger recombination current of diodes of #B epiwafer in the whole range of voltage are mainly due to the lower potential V_{bis} at the perimeter. In figure 3.6 the built-in potential at surface for #A epiwafer is around 0.16V which is a very low barrier compared to the 1.39V built-in at bulk (1.34V for bulk and 0.14V for surface for #B epiwafer). The different potential distribution is due to the difference in the base doping level and thus the surface channel characteristics. In the case of #B epiwafer the depletion layer from the n-type region (emitter) to the p-type region (base) is more extended into the latter when the doping level of the base is lower. For #A epiwafer the surface channel width for the region where the maximum band bending occurs at equilibrium (at the base of the diode) is around 60 nm while for #B epiwafer increases to 160 nm. The surface channel of the emitter for both epiwafers is around 70 nm. Therefore, the space charge region created at the surface is larger for diodes of #B epiwafer. Consequently, the higher the doping level the higher the amplitude of the bending. The lower the doping level the wider the surface channel.

Figure 3.9: Semi-logarithmic 3-D plot of recombination rate at the p-n junction for #A (left) and #B (right) epiwafers under forward bias: a) 0.7V, b) 1V and c) 1.3V. The depth and width (x coordinate) of the structure sides is shortened for simplicity.

The effect of the wider space charge region in perimeter recombination is shown in figure 3.9. For both epiwafers the higher recombination occurs where the junction space charge region intersects the perimeter as Dodd et al. [Dod+91] stated. For #A epiwafer the peak of recombination occurs exactly at the intersection of the p-n junction with the perimeter which is not the case for #B epiwafer where highest values are found at the p-n junction intersection but the peak is shifted a few nanometers into the base due to the larger space charge region. The same fact applies for the bulk recombination in both sides of the junction. The peak of recombination occurs at the location where there is a maximum availability of carriers (the highest np product).

In order to know the dominant recombination types, figure 3.11 shows the contribution of

Figure 3.10: Experimental measurements of the dark I-V curve for two representative diodes ($P/A=160$) manufactured on #A and #B epiwafers showing the influence of the base doping level. The blue line corresponds to the current ratio of both diodes as a function of the bias.

some recombination mechanisms as a function of the bias voltage for both epiwafers. As can be seen, perimeter recombination is dominant up to $V=1.1\text{V}$ (#A) and $V=1.2\text{V}$ (#B). Therefore, perimeter recombination can extend its influence to high voltage biasing, being highly dependent on bulk doping level.

3.2.1.7 Influence of perimeter recombination on GaAs concentrator solar cells

In this section, the model is used to discuss some of the key factors that affect perimeter recombination of GaAs concentrator solar cells. It must be noted that we do not pretend to carry out an exhaustive solar cell optimization but to show some case studies. First, we analyse the influence of pn junction doping level followed by the size and geometry of the solar cells.

Doping influence

The optimum base doping level for GaAs concentrator solar cells is a trade-off between series resistance, recombination current density and photogeneration current. While having a highly doped base provides a low resistivity it will reduce the photogeneration current by decreasing the electron diffusion length (the radiative and SRH lifetimes are better at lower dopant concentrations). Reducing the doping level will increase the electron diffusion length in base, but as we have seen, at low doping levels perimeter recombination could be important depending on the size of the device. Therefore, a further reduction of the base doping level could be useless without avoiding perimeter recombination. In order to assess the influence of base doping levels, simulations were performed from 10^{16}cm^{-3} to $4 \cdot 10^{18}\text{cm}^{-3}$ (figure 3.12) while

Figure 3.11: Simulation of the recombination rate contribution for radiative and non-radiative processes for a P/A=160 diode: a) #A epiwafer and b) #B epiwafer. Auger recombination is negligible with respect to the other recombination mechanisms so, for the sake of simplicity it is omitted.

keeping constant the rest of parameters from table 3.3. As can be seen, as the doping level increases the recombination current reduces by a factor of 10 (when comparing $N_A = 10^{16} \text{cm}^{-3}$ and $4 \cdot 10^{18} \text{cm}^{-3}$) from low bias until 1.1V (mainly because of the perimeter recombination influence) and after this value the current increases by a factor of 1.5 (this factor corresponds to the maximum difference at 1.2V). At high biasing (after 1.1V), the radiative recombination current is more dominant than the perimeter one while increasing the doping level, due to the larger carrier concentration and the reduction of perimeter recombination current (see general trends of figure 3.12). Thereby, when the base doping level is increased, the total current approaches to a kT -behaviour because of a dominant radiative recombination component. In the case of the emitter doping level variation (not shown here) the difference in total current is very low (assuming n/p structures with typical doping levels in base and emitter). Therefore, the main contribution to dark current comes from the base region.

Figure 3.12: Simulated dark I-V curve of a GaAs solar cell with a size of 0.01 cm^2 ($P/A=40$) varying the p-base doping level.

Size influence

In order to quantitatively account for the contribution of perimeter recombination on different solar cell sizes, the boundary condition at the surface ($N_t=0$, from equation for lifetime values included in equations 2.28 and 2.29) is removed to separate the influence of bulk and perimeter surface current. The evolution of both currents for a $P/A=40$ (0.01cm^2) square solar cell is shown in figure 3.13.

Figure 3.13: Simulation of the contribution of bulk and perimeter currents for a solar cell with a size of 0.01 cm^2 ($P/A=40$) manufactured on epiwafer #A.

Table 3.4 summarizes the transition voltage values where the bulk recombination current

equals the perimeter one and where the bulk current becomes dominant being five times greater than the perimeter one.

Table 3.4: Voltage values where bulk current (I_b) is equal and five times greater than perimeter current (I_p) for different solar cell sizes.

P/A(cm ⁻¹)	Area (cm ²)	Voltage (V)			
		$I_b = 5 \times I_p$		$I_b = I_p$	
		#A	#B	#A	#B
160	0.00625	>1.3	>1.3	1.229	1.264
40	0.01	1.264	>1.3	1.011	1.229
13	0.09	1.205	1.271	0.929	1.191
10	0.16	1.183	1.26	0.913	1.178
5	0.64	0.999	1.233	0.899	1.121
4	1	0.992	1.224	0.88	1.097

For smaller sizes of square solar cells the perimeter recombination has a strong influence on the whole voltage range. In fact, the smaller size ($6.25 \cdot 10^{-4}$ cm²) analysed shows that perimeter recombination current is the one that dominates the whole dark I-V curve. Even for larger sizes (1 cm² for square solar cells) the perimeter current dominates until 0.88V for #A epiwafer. In the case of solar cells on #B epiwafer even the larger sizes are strongly affected by perimeter recombination. For concentrator solar cells, the determination of the optimum size is a trade-off between the series resistance, perimeter recombination and the capacity to remove the heat away from the solar cell [Alg07]. Therefore, this study will contribute to such optimization.

Geometry comparison

In order to evaluate the solar cell geometry influence on dark I-V curves, figure 3.14 shows the current density ratio between square and circular devices ratio as a function of solar cell P/A and for two bias voltages. The voltages analysed are not affected by series resistance (neglected) and they are intended to show the performance of different solar cells when perimeter recombination dominates (0.7V) and when they are close to the typical operation point of GaAs solar cells (1V).

As figure 3.14 shows, square devices exhibit less recombination current for any size at 0.7V. At 1V, the difference between both geometries decreases with the P/A ratio. When comparing

Figure 3.14: Simulated dark current density ratio between square and circular devices as a function of their P/A for two bias voltages. Lines are a guide to the eye.

different device geometries the crystallographic orientation-dependence in perimeter recombination becomes important. The work of Stellwag [Ste+90a] showed that perimeter recombination could be reduced if the mesa-isolation process is properly oriented to the crystallographic axes of the device. Therefore, a given device presents different perimeter properties according to each orientation side of its mesa etching. For square solar cells, two sides could be aligned and the other two misaligned to the flat edge of the wafer, thus, the latter will have higher perimeter recombination values. In the case of circular devices, the orientation to crystallographic axes is not well defined. Only a small portion of the perimeter could be completely oriented (much lower than square shapes) to the flat edge. Lower perimeter recombination for square devices than for circular ones was also found in [DA01].

The reason why at 1V bias voltage the difference between square and circular solar cells becomes lower than at 0.7V is the following. At 0.7V, perimeter recombination is dominant (see figure 3.13 and table 3.4) for all P/A considered in the figure 3.14. Square solar cells exhibit less perimeter recombination than circular ones because of the orientation-dependence. However, at 1V perimeter recombination influence is decreased and very dependent on P/A. In the case of a low P/A, bulk recombination starts to dominate over the perimeter one, thus, the blue line of figure 3.14 decreases as a function of P/A and the difference between both geometries becomes lower.

3.2.2 Model validation and analysis

The validation of the model was performed on a traditional n on p GaAs single junction solar cells grown by MOVPE. Their structural characteristics are depicted in Table 3.5. Details on the growth can be found elsewhere [Gar10]. Solar cells of 1 mm^2 active area were obtained. No anti-reflection coatings were deposited. A complete characterization of the devices was performed in two stages. The first stage of characterization serves to get reliable input parameters of the semiconductor structure to the simulation. This includes Epi-RAS, CV and XRD measurements in order to get the values of layer thicknesses, doping levels and to confirm the lack of any significant lattice mismatch at the interfaces. In a second stage, device characterization including QE (internal and external), dark and light I-V curves and concentration measurements were performed. For QE measurements, solar cells with busbar but without fingers were used to avoid additional uncertainty about the illuminated area. The multi-data fitting has been performed on devices without ARC since ARC highly smooths the impact of the optical behavior of the semiconductor layers (specially the front layers) of the solar cell. In general, an excellent agreement is accomplished for all experimental data and the full list of used parameters is listed in Appendix A.

Table 3.5: Semiconductor layer structure of the GaAs solar cell.

Layer	Material	Thickness (nm)	Doping (cm^{-3})
Cap 1	GaAs:Te	174	$2 \cdot 10^{18}$
Cap 2	GaAs:Si	250	$2 \cdot 10^{18}$
Window	GaInP:Si	25	$1.4 \cdot 10^{18}$
Emitter	GaAs:Si	177	$1.1 \cdot 10^{18}$
Base	GaAs:Zn	3696	$1.2 \cdot 10^{18}$
BSF	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{As:C}$	150	$\sim 2 \cdot 10^{18}$
Buffer	GaAs:Zn	1000	$\sim 10^{18}$
Substrate	GaAs:Zn	350000	$\sim 10^{19}$

Fig. 3.15 shows the dark I-V curve together with the recombination contribution from different regions inside the solar cells. Perimeter recombination dominates up to values $\sim 1 \text{ V}$ and radiative recombination starts to be comparable to SRH recombination at 1.1 V . The orange filled square line shows the case where Shockley-Read-Hall (SRH) recombination is neglected and can be considered as the radiative limit on this particular design.

Figure 3.15: Experimental and simulated dark I-V curve of the GaAs solar cell together with the contribution from radiative and non-radiative recombinations.

The QE contributions shown in Fig. 3.16 are distributed among the three typical main regions, namely the emitter, base and SCR. The carrier collection efficiency is shown in brackets and only the window exhibits a low value, as expected due to surface recombination and low minority carrier properties. A third of the total QE comes from the base while the SCR is lower than the contributions from base or emitter. As in the case of dark I-V curves, the QE limitation of both solar cells is mainly due to SRH recombination

As mentioned previously, almost all layers have excellent collection efficiencies, except the window. As devices are intended to exploit the full solar spectrum, it is useful to bear in mind how much gain could be achieved if we improve the collection properties of the window layer and avoid surface recombination. As can be seen in Fig. 3.17, the EQE at the window can be significantly increased by improving its surface recombination or its collection properties. For instance, if we assume a perfect collection for the AM0 spectrum with a higher content of high-energy photons, a short-circuit current of about 3 mA/cm² can be collected at the window. This is roughly three times the value shown by the current structure. Surface recombination contributes about 65% of the losses and the rest are attributed to the poor minority carrier properties at the window. If an AlInP window is used instead of GaInP, the gain is still significant but it is diminished because of the higher transparency of this material. A similar relationship can be expected for the GaInP solar cell which is the material used as top cell in many multijunction structures.

A summary of the light I-V parameters is shown in Table 3.6. In some cases, SRH recom-

Figure 3.16: Experimental internal and external quantum efficiency together with the calculated contribution of different regions of GaAs solar cell with standard design. Bottom: Reflectance of the same solar cell structure. Symbols are used for experimental data while lines for simulations. The calculated depletion layer width is 230 nm. Carrier collection efficiency for each layer is shown within brackets.

Figure 3.17: EQE contribution of the window layer for three different cases: 1) current devices (green), 2) assuming no surface recombination (red) and 3) assuming complete or ideal collection (blue). Solid lines correspond to GaInP window layer while dashed lines correspond to an AlInP window layer.

bination has been neglected to show its impact on the performance. For GaAs at open circuit conditions (OCC), the main losses come from perimeter recombination that accounts for 31 mV

while the base (bulk) accounts for other 35mV. This design has an upper V_{oc} limit of 1043mV by neglecting all non-radiative recombination losses ($\tau \rightarrow \infty$ @all). In this instance, radiative recombination is dominant and photon recycling plays a key role to further increase the V_{oc} to reported values (~ 1.12 V) [Ste+13a]. At short circuit conditions (SSC), about 2 mA/cm² of J_{sc} are lost at the surface and window/emitter interface. When compared to GaAs solar cells with AlInP window, about 1 mA/cm² increase is expected while the rest 1 mA/cm² is lost by surface recombination. At OCC, there is a high limitation from the base and almost negligible from the emitter.

Table 3.6: I-V parameters for experimental and simulated GaAs solar cells at one sun under the AM1.5d ASTM-G173 direct spectrum. The I-V parameters under certain assumptions avoiding specific losses (SRH) are also shown. The minority carrier lifetimes assumed infinite correspond to simulations neglecting the non-radiative recombination (SRH). V_{oc} values would increase about 10 mV by considering ARC deposition.

I-V Parameter	Exp.	Sim.	$\tau \rightarrow \infty$ @all	$\tau \rightarrow \infty$ @base	$\tau \rightarrow \infty$ @emitter	No loss @win./emi.	No loss @per
J_{sc} (mA/cm ²)	19.81	19.75	21.66	19.88	19.76	20.28	19.75
V_{oc} (mV)	967	970	1043	1037	1003	973	1001
FF (%)	82.24	82.19	88.6	88.4	87.6	82.14	87.6

The validation of the model has been also carried out under light concentration. An excellent agreement is displayed in Fig. 3.18

Finally, to illustrate the influence of perimeter recombination at different light concentrations, simulations at 1 sun and 700 suns were carried out. Fig. 3.19 shows the 3D plot of current density at 1V. The current flows mainly through the perimeter region at low concentrations (1 sun) while at high concentrations (700 suns) the current is spread through the window layer until it reaches the metal regions. The evolution of V_{oc} and other solar cell parameters with light concentration will be discussed in Chapter 4 where a 3J multijunction solar cell will be analysed.

Figure 3.18: Experimental and simulated I-V standard GaAs solar cell parameters as a function of light concentration.

Figure 3.19: Current density of a quarter of a 1mm² GaAs solar cell at 1V for 1 sun (a) and 700 suns (b).

3.3 Analysis of GaInP solar cells

Typically ternary alloys have been used widely in heterostructure systems for optoelectronic devices. For instance, GaInP exhibits many advantages over other III-V semiconductors such as AlGaAs, namely: 1) selective etching regarding GaAs using acid solutions; 2) trap levels associated to oxygen are not typically found in GaInP, e.g., DX centres that have been commonly related to Aluminium in AlGaAs alloys [LLJ79; Bou90]; 3) band discontinuity in GaInP/GaAs

has been measured to occur mostly on the valence band, thus the potential barrier associated to majority carriers may not be an issue in multijunction solar cells; 4) the presence of In inhibits carbon incorporation when grown by MOVPE; 5) Very low recombination velocities at the interface have been measured for GaInP/GaAs heterostructures [Ols+89; Kur+99], among others. In general higher quality material can be obtained from GaInP alloys than AlGaAs ones.

Regarding its performance as solar cell absorber, outstanding luminescent properties have been measured and very high bandgap-offset voltages¹ ($W_{OC} \sim 360$ mV) have been reported for n-type GaInP solar cells [Gei+13]. This results in a very attractive pathway for improvement, however, most of the state-of-the-art solar cells are regarding p-type absorbers and this is the type of solar cell analysed here.

3.3.1 Model validation and analysis

The validation of the model was performed on a traditional n on p GaInP (partially ordered) single junction solar cells grown by MOVPE. Their structural characteristics are depicted in Table 3.7. Details on the growth can be found elsewhere [Gar10]. Solar cells of 1 mm² active area were manufactured. No anti-reflection coatings were deposited.

Table 3.7: Semiconductor layer structure of the GaInP solar cell.

Layer	Material	Thickness (nm)	Doping (cm ⁻³)
Cap	GaAs:Si	420	$> 1 \cdot 10^{19}$
Window	AlInP:Si	20	$8 \cdot 10^{17}$
Emitter	GaInP:Si	150	$8 \cdot 10^{17}$
Base	GaInP:Zn	550	$1 \cdot 10^{17}$
BSF	AlGaInP:Zn	75	$\sim 5 \cdot 10^{17}$
Buffer	GaAs:Zn	1300	$\sim 10^{18}$
Substrate	GaAs:Zn	350000	$\sim 10^{19}$

Fig. 3.20 shows the dark I-V curve along with the recombination contributions from different regions. The dark I-V curve of GaInP is mainly controlled by non-radiative recombination, being the base region (including depleted and quasi-neutral regions) the one that dominates the

¹ W_{OC} is defined as the difference between the bandgap of the material and the measured open circuit voltage of the solar cell.

curve even at high bias (1.45V). Radiative recombination is too low compared to SRH recombination at any voltage. The orange filled square lines show the case where Shockley-Read-Hall (SRH) recombination is neglected and can be considered as the radiative limit on this particular design.

Figure 3.20: Experimental and simulated dark I-V curve of the GaInP solar cell whose structure is shown in Table 3.7 together with the contributions from radiative and non-radiative recombination.

The QE contributions shown in Fig. 3.21 are distributed again in the emitter, base and SCR. The carrier collection efficiency is shown in brackets where only the window exhibits low collection efficiency, as expected due to surface recombination and low minority carrier properties. A third of the total QE comes from the base and the SCR is lower than the contributions from base or absorber. As in the case of dark I-V curves, the QE limitation is mainly due to SRH recombination.

A summary of the light I-V parameters is shown in Table 3.8. In some cases, the SRH recombination has been neglected to show its impact on the performance. At SCC, there is lower J_{sc} improvement than GaAs shown in previous sections mainly because the window layer is thinner and it is compared to different window material (GaInP in the case of GaAs solar cell). When comparing to GaAs solar cell with AlInP window, the gain is similar, 0.7mA/cm² and 1mA/cm² for no ARC and with ARC, respectively. At OCC, there is a high limitation from the base and almost negligible from the emitter. This result shows that, for this particular design, the removal of a highly doped and defective emitter may not be behind the improvement of the n-type rear heterojunction solar cells demonstrated in [Gei+13].

Figure 3.21: Experimental internal and external quantum efficiency and the calculated contribution for the GaInP solar cell. Bottom: Reflectance of the same solar cell structure. Symbols are used for experimental data while lines for simulations. The BSF contribution is not zero mainly because the total thickness of the solar cell does not absorb 100% of light. Depletion layer width is 336 nm. Carrier collection efficiency for each layer is shown within brackets.

Table 3.8: I-V parameters for experimental and simulated GaInP solar cells at one sun under the AM1.5d ASTM-G173 direct spectrum. The I-V parameters calculated under certain assumptions avoiding specific losses (SRH) are also shown. The minority carrier lifetime assumed infinite corresponds to simulations neglecting the non-radiative recombination (SRH). V_{oc} values would increase about 10 mV by considering ARC deposition.

I-V Parameter	Exp.	Sim.	$\tau \rightarrow \infty$	$\tau \rightarrow \infty$	$\tau \rightarrow \infty$	No loss @win./emi.
			@all	@base	@emitter	
J_{sc} (mA/cm ²)	10.70	10.83	11.49	10.84	11	10.84
V_{oc} (mV)	1369	1371	1451	1447	1372	1371
FF (%)	86	85.9	91.1	90.7	86.2	85.9

3.3.2 Design flexibility for multijunction solar cells by tuning the GaInP bandgap

GaInP is typically used as the top cell of many multijunction solar cells such as state-of-the-art GaInP/Ga(In)As/Ge solar cells, inverted metamorphic GaInP/Ga(In)As/GaInAs solar cells, or

GaInP/Ga(In)As/GaInAsN solar cells as well as top junction in 4J solar cells (see for instance Chapter 5). The preferred tuning parameter in multijunction solar cells to optimize the structure for a better utilization of the spectrum is the bandgap of materials. In the case of GaInP, it is possible to increase the bandgap — while preserving lattice-matching conditions — with the use of Sb to disorder the GaInP [OMK07]. Therefore, by increasing the bandgap of GaInP solar cells their V_{oc} is enhanced but their photocurrent get reduced due to the lower cut-off wavelength in the absorption coefficient of the material.

To increase the efficiency of the GaInP solar cell, one must raise the V_{oc} while keeping the photocurrent as high as possible. To preserve the multijunction current matching, the top cell thickness base is typically used as an adjustable parameter [KFO90]. However, a base thickness increase leads to a V_{oc} decrease. Accordingly, Figure 3.22 illustrates the solution of this trade-off for solar cell architectures in which GaInP lattice matched to Ge (or GaAs) is used as the top cell. In particular, Figure 3.22 depicts the evolution of J_{sc} and V_{oc} as a function of thickness and E_g of the base layer in the GaInP subcell for a typical GaInP/Ga(In)As/Ge 3J solar cell under AM1.5d ASTM G173-03 spectrum. The bandgap range considered is something attainable by controlling the ordering around the GaInP composition considered in the example. For the simulation, it has been considered that: 1) the photogeneration of carriers is zero for photons with energies below E_g and 2) there is no degradation of the minority carrier properties due to the use of Sb. As can be seen in Figure 3.22(a), the J_{sc} is very sensitive to the base thickness, especially for low values of E_g .

A J_{sc} gain of around 3 mA/cm² can be obtained by increasing the base thickness from 300 to 1600 nm for low bandgaps (1.8-1.84 eV). For mid-high bandgaps, a lower increase is expected (about 1.5 to 2 mA/cm²). Regarding V_{oc} (Figure 3.22(b)), the highest values are expected for high E_g and relatively thin base thicknesses (300-700 nm). For example, for a base thickness of 500 nm a gain of 50 mV is feasible by increasing E_g from 1810 to 1880 meV. However, as the base thickness must be as high as possible to keep the same current levels when using high bandgaps, the dark saturation current is also increased, and consequently, V_{oc} is reduced. Nonetheless, the net change in V_{oc} due to the increase of E_g and base thickness is positive, which justifies the procedure. Besides, the kT -recombination current impacts on V_{oc} gets reduced as the bandgap is increased (almost negligible for $E_g > 1.88$ eV) due to a reduction of the intrinsic carrier concentration [SN06]. In summary, higher bandgaps are preferred in order to raise the V_{oc} together with a thicker base to adjust the photocurrent in any particular multijunction solar cell design.

Figure 3.22: (a) Calculated short circuit current density and (b) open-circuit voltage of the GaInP subcell latticed-matched to Ge as a function of the bandgap energy and the thickness of the base layer under AM1.5d ASTM G173-03.

3.4 Analysis of Ge subcells for advanced multijunction solar cells

Germanium is an important material for PV industry mostly used as the bottom subcell and mechanical support for the most mature III-V multijunction architecture, the commercially available GaInP/Ga(In)As/Ge 3J. It is not only important for this architecture but also considered as the bottom subcell of advanced multijunction solar cells relying on lattice matched structures (four to six junctions, see [Sua+17]). This is mainly because of its bandgap suitability and cost effectiveness in comparison with other architectures based on more expensive substrates (i.e. GaAs and InP, see for example [Fra+15; Dim+16], respectively).

The widest used technology for the development of Ge subcells for III-V multijunction solar cells is MOVPE². A successful development of a Ge solar cell in a MOVPE environment involves growth optimization that must ensure: 1) the growth of a defect-free polar III-V layer (nucleation layer) on a non-polar structure such as Ge; 2) good surface morphology and 3) successful emitter formation. This can be achieved by growth conditions (e.g. temperature, V/III ratio, etc.) and a careful surface preparation on mis-oriented Ge substrates [Bar+13].

Typically, Ge n-p junctions for III-V multijunction solar cells are formed by the in-diffusion of group-V elements —being the most common ones P and As diffused from the nucleation layer— into p-type Ge substrates. The emitter formation is a critical step very dependent on the

²Despite of the fact that MOVPE is the most used technology to develop Ge subcells, MBE has recently gain a lot of attention. Ge single junction solar cells grown by MBE have been recently reported ([MFL16]) resulting in useful devices with lower performance, but close to the Ge subcells (inside a 3J structure) presented in this section.

thermal load applied that controls the PV properties of the subcell and can significantly degrade its performance [FO01; Bar+18]. For example, *as-grown* Ge devices (grown as single junction solar cells with no extra thermal load from subsequent growth) typically perform much better than Ge subcells inside a 3J device. Indeed, Ge single junction solar cells usually have a V_{oc} in excess by tenths of mV (up to 55 mV measured in our Ge samples [Bar+18]) than Ge subcells inside a 3J [FO01; Kal+10; Hoh+13].

Accordingly, in this section we focus on two main targets: 1) to validate the modelling for Ge solar cells to be used in a multijunction structure and 2) to analyse the experimental results obtained in previous works³ for Ge solar cells subjected to different thermal loads by using the validated model..

3.4.1 Model customization for gradual emitters

Three Ge solar cells with different thermal loads (i.e. time and temperature) have been analysed⁴. Two of them correspond to single junction solar cells (*as-grown* devices), namely #A2 and #A3 with different growth temperatures for the nucleation layer (i.e. GaInP): 640°C and 675°C, respectively. The effect of the thermal load on Ge (emitter formation) coming from the subsequent growth of GaAs and GaInP top cells is studied on a third Ge solar cell, namely #E3 (*etched*), that was originally a 3J structure, but with the upper layers etched away to virtually obtain the same semiconductor layer structure than in single junction cases. The semiconductor structure for the three samples consists of a 500-1000nm contact layer (nominally doped $8 \cdot 10^{17} \text{ cm}^{-3}$), followed by a 300-1000nm nucleation layer (nominally doped 10^{18} cm^{-3}) and the Ge n-p junction. Measured resistivity for the p-type substrates (Ge base) results in values of 8.8, 9.5 and 20 mΩ·cm, respectively while the emitter properties will be discussed later. Solar cells with active area of 0.1 cm² were manufactured⁵ and no ARC was deposited onto the solar cells.

3.4.1.1 Model assumptions

When growing the GaInP nucleation layer, Ga, In and P atoms diffuse to Ge. The group-III (Ga and In) are p-type dopants in Ge while P acts as an n-type dopant. Because of the higher

³The experiments were led by E. Barrigón while all simulation analysis and modelling shown here was performed by the author of this thesis.

⁴MOVPE growth of this structures was carried out by E. Barrigón and the III-V growth team.

⁵Manufacturing, processing and electrical characterization of the solar cells was carried out by I. García at NREL facilities.

diffusion coefficient of P with respect to Ga and In (about two to three orders of magnitude [Dun54]), the n-type doped Ge is achieved. Indeed, P diffuses quickly via vacancy-mediated diffusion mechanisms to form the emitter [CB14]. Therefore, the n-type doping profile is expected to be non-uniform. For instance, Fig. 3.23 (bottom) shows three different emitter doping profiles corresponding to the three samples analysed. In general, according to Fick's laws, typical diffusion doping profiles show a decreasing curve with thickness (following a complementary error function) which does not occur in any sample as can be seen in Fig. 3.23 (bottom). In contrary, doping starts to increase until it reaches a maximum value (vertical dashed lines) and then the conventional diffusion profile is observed. The physical explanation to the gradual increase of doping at the beginning of the emitter lies on the fact that thermal load urges the indiffusion of Ga and In acting as p-type dopants [Gud+12; Bar+18]. The strength of this effect is such that is capable of reducing the n-type doping developed by P in the vicinity of the isotype heterojunction (GaInP/Ge). Indium is suggested – over Ga – as the main cause of the n-type doping reduction because of its higher diffusion coefficient (see [Dun54; Bar+18] and Fig. 3.22 of L. Barrutia PhD thesis [Bar+17]). Then, when the maximum doping value is reached (vertical dashed lines), a plateau is observed followed by the typical decreasing diffusion gradient profile.

To exemplify more clearly the region division and to describe the model assumptions, Fig. 3.23 (top) shows a schematic diagram of the layer structure together with different profiles of doping and material parameters assigned to the emitter (the rest of the layers are assumed with uniform properties). To feed the simulations, realistic material parameters need to be calculated for each region. To this end, the Ge solar cell is divided into three regions, two to model the emitter and a third one to describe the base. The first region, namely, emitter #1 (E_1 or gradual emitter, G_E) corresponds to the gradual emitter zone extending from the GaInP/Ge interface down to the depth where the highest doping level is reached (i.e. at the beginning of the plateau region in the ECV profile of the bottom graph in Fig. 3.23, i.e. the vertical dashed lines). This region is the zone where the three diffusion profiles of Ga, In and P coexist and influence the effective n-type doping in the germanium. The second region, namely, emitter #2 (or E_2), extends from the highest doping level to the junction depth (X_E). Analogously, this region represents the zone of the plateau and tail in the doping concentration where only the diffusion of P needs to be considered to explain the n-type doping profile in the Germanium. Finally the third region is just a p-type Ge slab with constant doping, corresponding to the base.

In the case of the first region (E_1 or G_E), we can expect a severe degradation of the emitter electronic properties due to the heavy dopant compensation (confirmed by bottom graph of

Figure 3.23: Top: Schematic of the baseline structure (not scaled to real dimensions) and model assumptions for the Ge emitter. Bottom: Non-uniform doping profiles at the Ge emitter used in the simulations (from ECV measurements) for the three samples analysed. The curves are shown from the beginning of the emitter until the junction depth is reached (i.e. $N_D = \text{BCC}$). Vertical dashed lines indicate the intersection of emitter #1 and #2 for each solar cell. X_E corresponds to the total emitter thickness, including E1 and E2.

Fig. 3.23 and SIMS measurements in [Bar+18]). In our model this region is simulated with a constant minority carrier diffusion length ($L_{h,E}$), which is the parameter swept in the following simulations. However, in emitter #2 and in the base of the Ge solar cell a much lower degree of compensation is expected and thus analytical models for minority carrier properties have been used. Doping dependence in the minority carrier diffusion length in emitter #2 departs from the $L_{h,E}$ value in emitter #1 to ensure material parameters continuity as can be deduced from Fig. 3.23 (top). In particular, expressions for the doping dependence of minority carrier lifetime were taken from [Gau+07] for both p-type and n-type Ge whilst those for carrier mobilities were obtained from [Pri53]. The same equations were used for holes as majority (p-type base) and minority carriers (n-type emitter #2), since to our knowledge, no empirical data for hole properties in highly doped n-type germanium can be found in literature. Noticeably, hole

properties in emitter #2 will vary with depth as a result of the gradient in dopant concentration, whereas electron properties in the p-type base will be constant throughout.

Bandgap narrowing in the highly doped n-type emitter was also accounted for using the analytical expressions obtained in [JR91]. Despite the fact that this expression was derived for uniformly doped materials and thus its accuracy may be limited when working with varying doping profiles [LB89], the good quality of the fits (see next section) obtained backed its applicability. Again as a result of the doping profile in emitters #1 and #2, a variable bandgap narrowing vs. depth is calculated in those layers which in turn yields a variable bandgap across the emitter. Finally, interface recombination velocity (S_E) between GaInP and Ge has been considered together with *infinite* surface recombination velocities at front and back contacts (i.e., ohmic contacts). Further details on the analytical expressions for material parameters employed can also be found in the Appendix A.1.3 of this document.

3.4.2 Model validation

Following our methodology for model validation, the typical PV characterization curves (EQE, IQE, R, dark and light I-V) of the three Ge solar cells have been successfully reproduced by the model by using exactly the same set of material parameters (see section 3.4.3.3) and model assumptions described previously. Fig. 3.24 shows the measurements (black solid squares) and simulation (red solid lines) results of IQE (top), EQE (middle) and R (bottom) for the solar cells analysed. The models and material parameters employed have been validated by simultaneously fitting the experimental IQE (by fitting independently the EQE and reflectance curves as shown in Fig. 3.24), light J-V and dark J-V curves as it will be shown later). It is worth to mention that the simultaneous fit for sample #E3 is only achieved by including the measured doping profiles.

QE degradation at low wavelengths (i.e. emitter region response) suffered by the effect of increasing the thermal load, as can be observed in Fig. 3.24. Thanks to the modelling, we are able to quantify the emitter contribution for each sample. Indeed, the emitter collection efficiency (CE) shown within brackets (pink numbers) reduces from 93% to 75% and 0% for #A2, #A3 and #E3, respectively. No significant changes have been observed and extracted from simulations regarding the contributions from the base region. In fact, for the most degraded case (#E3), the CE is higher (92%) than the best IQE (#A2 with 75%). This can be explained by the different resistivity measured in these Ge substrates samples. The resistivity of #E3 is almost twice than that of #A2 (20 and 8.8 mΩ·cm, respectively).

Performance degradation by thermal load did also appear in the I-V characteristics. As can be seen in Fig. 3.25, the total recombination current increased as a function of the thermal load

Figure 3.24: Experimental (black square filled symbols) and simulated (red solid lines) IQE (top), EQE (middle) and reflectance (bottom) curves for the three samples analysed in this section (i.e. #A2, #A3, #E3). The contributions of each region in the structure is also depicted for each IQE curve (dashed lines). The CE calculation (for $\lambda > 885\text{nm}$) is shown within brackets for the AM1.5d ASTM-G173 solar spectrum.

and the ideality factor (equal to 1) did not show any modification.

Figure 3.25: Experimental and calculated dark I-V curves for the three samples.

Finally, light I-V curves were measured in several devices under a 1-sun calibrated solar simulator and their parameters are shown in Table 3.9 for the three samples. All parameters were seriously affected by the thermal load. The highest V_{oc} drop measured was about 65 mV for champion cells #A2 and #E3. FF also dropped by 6% absolute. Measured and simulated I-V parameters of devices #A2, #A3 and #E3 are in good agreement as summarized in Table 3.9.

The highest deviation ($\sim 4\%$) occurs for the J_{sc} values of device #E3, which is explained by the worse fitting of the IQE from 440 to 700 nm (see Fig. 3.24). All in all, the multiple-fitting under different bias conditions achieves an excellent agreement with the experimental data.

Table 3.9: Measured and simulated J_{sc} , V_{oc} and FF of representative devices of structures #A2, #A3 and #E3. Experimental values correspond to the champion cells. Relative standard deviations for all measured devices (about 5-10 for each solar cell) were lower than 2% for J_{sc} and FF and within the range of 0.3-0.9% for V_{oc} .

Sample	J_{sc} (mA/cm ²)			V_{oc} (mV)			FF (%)		
	Exp	Sim	Deviation	Exp	Sim	Deviation	Exp	Sim	Deviation
#A2	20.7	20.7	0.00%	245	244	0.40%	66.8	67	0.30%
#A3	19.03	18.8	1.21%	211	212	0.47%	64.4	64.3	0.16%
#E3	17	16.3	4.10%	180	180	0.00%	60.5	60.8	0.50%

The reasons behind the degradation observed in both QE and V_{oc} in *etched* 3JSC devices may be the change in X_E and in the variation of the doping profile close to the III-V/Ge heterointerface (the gradual region), as experimentally observed in Fig. 3.23 (bottom). We also speculate that a change in the minority carrier diffusion length at the emitter ($L_{h,E}$) and in the nucleation/emitter interface recombination velocity (S_E) may have taken place. In order to identify or rule out the different mechanisms that may produce such degradation, we have performed simulations to determine: a) the impact of the gradual emitter shape and X_E , b) the influence of the minority carrier diffusion length at the emitter and S_E .

3.4.3 Impact of gradual emitter

3.4.3.1 Gradual emitter profile and emitter thickness

The electric field in a heterojunction between two different semiconductors results mainly from their band alignment, which can be modified by the doping level in each semiconductor. In the GaInP/Ge heterojunction that applies to this work, the particular doping profile created by the simultaneous diffusion of group V and III elements (i.e., the so called gradual emitter) modifies the conduction and valence band in the vicinity of the heterointerface, as depicted in the simulation shown in Fig. 3.26. This figure presents the conduction and valence band diagrams of an n-GaInP/n-Ge isotype heterojunction for three cases, namely, the two doping profiles presented in Fig. 3.23 and the ideal case of uniform doping. In other words, the band diagrams of Fig. 3.26 represent those of solar cells #A2 and #E3 (as representative solar cells of

as-grown and *etched* 3JSC devices, respectively) and a third case of constant doping included for comparison. As can be seen in the figure, a depletion region for electrons forms in the conduction band (Fig. 3.26a), whilst an accumulation region for holes appears in the valence band in the Ge side next to the nucleation/emitter interface. Such regions become larger for cases where the gradual doping profile extends wider (e.g., profile #E3). In the valence band, the accumulation region at the heterointerface confines minority carriers and pushes them towards the heterointerface where they readily recombine via interface states. In the conduction band, a depletion region is formed creating a potential barrier for majority carriers. Gudovskikh et al. suggested the presence of a p-type region between the GaInP window and the Ge emitter as the origin of the potential barrier of around 120 meV formed at their samples [Gud+12]. In this work, we find that the gradient in the effective carrier concentration at the emitter interface is by itself capable to produce significant barriers (i.e. 17 meV for an *as-grown* sample and 66 meV for an *etched* one). Indeed, by considering interface recombination (analysed later) the modification of charge at the interface produces such high barriers (up to 250 meV depending on the amount of charge accumulation) that covers the values reported by Gudovskikh et al. [Gud+12].

Figure 3.26: (a) Conduction band energy at equilibrium for different experimental emitter doping profiles. (b) Valence band energy at equilibrium for different experimental emitter doping profiles.

In order to quantify the impact of these different band diagrams (structures #A2 and #E3) on the electrical performance of the Ge subcells, the corresponding J-V curves were simulated. As

a first approach, the emitter minority carrier diffusion length and S_E values of structure #A2 (0.6 μm and $1.5 \cdot 10^4$ cm/s, respectively) were assumed for both structures. In this respect, this first simulation allowed us to assess the isolated influence of the emitter characteristics (i.e., doping gradient and thickness) on the V_{oc} of the devices. Under these assumptions, the difference in the calculated V_{oc} between profile #A2 and #E3 was only 10 mV (247 and 237mV, respectively), much less than observed experimentally (see Table 3.9). If the simulation is repeated with the same X_E (280 nm) in both cases, but keeping their corresponding gradual emitter, it yields 9 mV loss for V_{oc} . In summary, neither the increase in X_E nor the shape of the gradual emitter fully explain the degradation in V_{oc} experimentally observed for *etched* 3JSC devices.

3.4.3.2 Impact of S_E and minority carrier properties at the emitter

In addition to the emitter depth and doping profile there are other phenomena associated with the diffusion taking place that may influence the collection properties of the emitter. To name the most relevant, we have 1) the formation/evolution of new surface states at the GaInP/Ge heterointerface; 2) the widening of the hole accumulation region explained in Fig. 3.26; and 3) the increase in the concentration of defects or minority carrier traps in the emitter region. Effects 1) and 2) would increase the effective surface recombination velocity at the emitter (S_E) whereas effect 3) would reduce its minority carrier (hole) diffusion length ($L_{h,E}$).

Therefore, to explore how variations in S_E and $L_{h,E}$ affect V_{oc} and J_{sc} of the Ge subcell we calculated the contour maps shown in Figure 3.27. Figure 3.27 (a) and (b) are contour plots of J_{sc} and V_{oc} , respectively, as a function of $L_{h,E}$ and S_E in emitter #1 for the *as-grown* device #A2. For this sample, the measured X_E was 180 nm, being the doping upsurge zone gradual emitter (emitter #1) 40nm deep and the plateau-tail zone (emitter #2) 140 nm thick. The thick dashed lines in Fig. 3.27(a) and (b) represent the iso- J_{sc} and iso- V_{oc} curves that match the experimental values measured for structure #A2 (see Table 3.9). Focusing on the current, in the iso- J_{sc} contour for 20.7 mA/cm² that applies to sample #A2 we have the following situation: the value of the minority carrier diffusion length stays fixed at $L_{h,E} \sim 0.45 \mu\text{m}$ for low values of S_E (horizontal stretch of the contour) whereas for high values of $L_{h,E}$, the surface recombination velocity stays fixed at $S_E \sim 3 \cdot 10^4$ cm/s (vertical stretch of the contour). In other words, in the horizontal stretch, the collection is limited by the value of the diffusion length and is insensitive to the low surface recombination velocity. In the vertical, stretch it is a high value of S_E which determines the amount of carriers lost at the surface (and thus collection) and $L_{h,E}$ has no impact since it has a value high enough to collect all remaining carriers. A similar discussion could be stated for V_{oc} maps in Fig 3.27(b).

Figure 3.27: Simulated J_{sc} (a and c) and V_{oc} (b and d) as a function of the effective S_E and $L_{h,E}$ of structures #A2 (a and b) and #E3 (c and d) with their corresponding emitter characteristics (i.e., gradual emitter and thicknesses). Dashed thick lines indicate the range of values that fit experimental V_{oc} and J_{sc} independently, while the yellow stars stand for the overlapping of the dashed thick lines corresponding to the best data fitting.

According to the latter explanation, an upper bound for S_E and a lower threshold for the $L_{h,E}$ can be established for sample #A2. Even more so, since the maps for J_{sc} and V_{oc} are calculated independently, the combinations of $L_{h,E}$ and S_E that fit the experimental J_{sc} and V_{oc} do not need to be exactly the same, i.e., the thick dashed curves in Figs. 3.27(a) and 3.27(b) do not exactly overlap. Therefore, the intersection between those curves, represents the set of possible $(L_{h,E}, S_E)$ that have physical meaning for structure #A2. The overlap for the best fit occurs at the points marked with a yellow star in Figures 3.27(a) and 3.27(b) and allows to further reduce the range of S_E and $L_{h,E}$ ranges that fit the results of sample #A2. Analogously, Figure 3.27(c) and (d) are contour plots of J_{sc} and V_{oc} for the *etched* 3JSC device #E3, again as a function of $L_{h,E}$ and S_E . In this case, the additional thermal load produces an increased X_E of about 100 nm, being the doping upsurge gradual emitter 90 nm deep, whereas the plateau-tail zone was of about 190 nm. Again, the thick dashed lines represent the iso- J_{sc} and iso- V_{oc} that match the experimental values measured for structure #E3 (see table 3.9), and their overlapping corresponding to the best fit has been also marked with a yellow star. In this case, the iso- J_{sc} contour of 16.3 mA/cm² and the iso- V_{oc} curve of 180 mV that fit the experimental result do

not look any more as rounded corners but almost as flattened s-shaped curves or almost straight lines running parallel to the x-axis. This reveals an (almost) total insensitivity to S_E and a sole dependence on a very small diffusion length of $L_{h,E} \sim 0.14 \mu\text{m}$. In this way, the interpretation of the degradation process behind the thermal load is straightforward: a severe degradation of the minority carrier collection properties occurs in emitter #1. All in all, the simulations show that hole properties of the n-type Ge emitter in the vicinity of the GaInP/Ge heterointerface are the main responsible for the recombination losses within the structure and are limiting the V_{oc} of the devices. In fact, according to the simulations, the base accounts for just 16% of the total recombination losses for the *as-grown* case whereas it drops to about only 3% for *etched* devices.

3.4.3.3 Sensitivity analysis

As deduced from Fig. 3.27, several sets of material parameters are able to fit —within a reasonable range of deviation— the I-V characteristics. This can be achieved by playing around with parameters S_E and $L_{h,E}$, however, there may be also additional uncertainties in the mobility of minority carriers within the emitter (since there is no experimental data for such a high doping concentrations available in the literature). Moreover, other physical mechanisms occurred within the emitter #1 (that inhibit the electrical activation of phosphorous as dopant) could also affect the mobility of carriers. Because of this fact, a sensitivity analysis for different S_E , $\tau_{h,E}$ and minority carrier mobility ($\mu_{h,E}$) at the emitter was performed. Again, $\mu_{h,E}$ and $\tau_{h,E}$ have been only assigned to emitter #1 and represent an effective mobility and lifetime of carriers within that zone.

The dominant V_{oc} losses come from the interface recombination at GaInP/Ge(emitter) through parameters (S_E and $L_{h,E}$) as depicted in Table 3.10 where the highest contribution from the base is only 16% (#A3). Thus, the emitter controls the device performance in both, *as-grown* and *etched* solar cells.

For *as-grown* solar cells, it is not possible to confirm that both parameters (S_E and $L_{h,E}$) contribute to the overall recombination losses, since the experimental I-V characteristics can be actually explained by degrading only one of them (either by contributing 0 or $\sim 83 - 85\%$). However, it is reasonable to expect that both parameters are affected by thermal degradation, but with the present results we are unable to quantitatively determine it.

A degradation of the minority carrier properties at the emitter is required to explain the experimental results in *etched* solar cells. This means that one can ponder about new designs capable of avoiding any of those parameters with the certainty that some improvement can be

Table 3.10: Fraction of recombination losses for different scenarios at the interface window/emitter (W/E), emitter (E) and base (B) under dark conditions (close to virtual open circuit voltage) for samples analysed in this section (#A2, #A3 and #E3). The range of values extracted from the sensitivity analysis for $\mu_{h,E}$, $\tau_{h,E}$ and S_E is shown. The scenarios involve cases for maximum and minimum threshold values of $\mu_{h,E}$ and considering infinite or absence of interface recombination between window and emitter. The range of values extracted was established by assuming that the multiple data fitting for J_{sc} (keeping similar IQE shape) and V_{oc} did not deviate more than 2% and ± 2 mV, respectively. The diffusion length for electrons at the base (L_b) is also depicted. The emitter and base losses were obtained by integrating the recombination rate over each region including the space charge region in each zone.

Sample	Case	Recombination losses at region	Material parameters									
			Min. Mobility			Max. Mobility						
		W/E	E	B	Other	$\mu_{h,E}$ ($\text{cm}^2/\text{V}\cdot\text{s}$)	$T_{h,E}$ (ns)	S_E (cm/s)	$\mu_{h,E}$ ($\text{cm}^2/\text{V}\cdot\text{s}$)	$T_{h,E}$ (ns)	S_E (cm/s)	L_b (μm)
#A2	$S_{E,min}$	0%	83%	16%	1%	200	0.15	0	900	0.04	0	23
	$S_{E,max}$	83%	0%			>10	$5\cdot 10^4$			>10	$4.5\cdot 10^4$	
#A3	$S_{E,min}$	0%	85%	9%	6%	350	0.04	0	900	0.04	0	28
	$S_{E,max}$	85%	0%			0.1	$1.25\cdot 10^5$			>10	$1.5\cdot 10^5$	
#E3	$S_{E,min}$	16%	77%	3%	3%	350	0.01	$1.25\cdot 10^5$	650	0.02	$2.5\cdot 10^5$	85
	$S_{E,max}$	54%	40%			0.01	$>6.5\cdot 10^5$			0.02	$>6.5\cdot 10^5$	

obtained. This suggests that the thinning of the emitter would be beneficial despite the presence of high density of traps at the interface⁶.

The range of values suggested for the material parameters can be extended if larger deviations from experimental results are taken into account (deviations lower than 2% for J_{sc} and ± 2 mV for V_{oc} were considered). However, special cautions were taken to avoid additional uncertainties in the measurements, mainly to control precisely the temperature as well as the use of calibrated solar simulator for 1-sun measurements. Indeed, the threshold assumed achieves good data fitting taking into account the relative standard deviations measured for all samples.

The full list of material parameters range shows an important fact: $\mu_{h,E}$ has an unexpected impact on the V_{oc} . This occurs for #A3 when a maximum S_E is considered and for #E3 independently of S_E . For example, by comparing the material parameters for different mobilities in #E3 and maximum S_E , it is observed that if $\mu_{h,E} = 650 \text{ cm}^2/\text{V}\cdot\text{s}$, $\tau_{h,E}$ must double its value (from 0.01 to 0.02 ns) in order to fit the data. By increasing $\mu_{h,E}$, QE gets enhanced as expected, but it degrades V_{oc} . Therefore, $\tau_{h,E}$ must also be increased in order to fit the data. The reason why mobility affects open circuit voltage can be explained by its contribution from dark recombination at V_{oc} in the vicinity of the interface and the asymmetry between E1 and E2 in terms of minority carrier lifetime, being lower for E1 as described previously. Carriers are able to move faster from emitter E2 to the interface (GaInP/Ge) rather than towards the junction if a higher mobility is assumed, thus favouring interface recombination and the recombination at E1. If mobility is lower, the chances to reach the interface or E1 diminish. The effect of mobility on V_{oc} is highly reduced on as-grown structures such as #A2 and #A3. Indeed, although the mobility is higher in these cases, holes *live* longer also in E1 giving higher chances to cross the junction and avoiding interface recombination. To illustrate this effect, Fig. 3.28 shows the integrated recombination rate along a portion of the structure for a high and low mobility cases at a fixed voltage of 160 mV (close to the maximum power point). The V_{oc} difference between these two cases is about 25mV, being higher for the low mobility case. As can be seen, recombination rate starts to be higher for the high-mobility case at the vicinity of the nucleation layer and emitter 1 interface. At E1 it shows almost constant values while at E2 increases slightly, but always being higher than the low-mobility case. The fact that E1 shows almost a constant high value indicates that the recombination rate at that region does not suffer significant changes with respect to the values obtained close to the interface, thus its recombination (high) is comparable

⁶Pathways to increase V_{oc} by modifying reactor conditions, e.g. using shorter nucleation routines could be found in PhD thesis of L. Barrutia [Bar17]

to the one at the interface.

Figure 3.28: Integrated recombination rate values at 160mV for *etched* solar cell #E3 with two different hole mobilities at E1. Layer notation is that of Fig. 3.23.

Finally, L_b shows consistency with the fact that higher CE's (as shown in Fig. 3.24) have been extracted for *etched* devices mainly because the lower doping concentration measured.

3.4.4 Recovery of V_{oc} with light concentration

Fig. 3.29 shows the V_{oc} (experimental and simulated) as a function of light concentration for the three samples analysed. Simulations predict a single slope logarithmic dependence (at different magnitudes) of V_{oc} with light intensity as typical in solar cells. This trend (single slope) is followed reasonably well for the #A2 (blue squares). Interestingly, for #E3 (*etched* shown in red circles), two slopes are clear. One corresponding to low light concentration regime (below 40 suns) and a second one above 40 suns. Maximum deviation from simulation of 25 mV is observed for the highest concentration measured for this device (436 suns). Despite two slopes can also be inferred for the #A3 device (*as-grown* at higher temperature than #A2), the maximum deviation from simulation is significantly lower than #E3 (5 mV).

Accordingly, V_{oc} of *as-grown* devices that did not suffer further degradation due to thermal load (i.e. #A2) follows a logarithmic trend with light concentration while *etched* devices show a significant recovery of V_{oc} with light concentration. Different slopes were not found in their dark I-V curves, suggesting that the main reason behind this recovery may be attributed to different behaviour when current is flowing in one direction or another (i.e., dark or illuminated). We also speculate that it may be attributed to a dependence of the minority carrier lifetime as a function of the injection level. This should come from the emitter because these devices are

Figure 3.29: Simulated (lines) and experimental (symbols) V_{oc} as a function of light concentration for the two as-grown samples (#A2 and #A3) and the etched one (#E3).

SRH-emitter-limited as shown previously. In any case, the modelling used here did not capture the V_{oc} recovery whose origin is still unknown and under investigation.

3.5 Tunnel junctions data fitting

Local models were not able to reproduce most of the experimental data available⁷ for most of the tunnel junctions developed for multijunction solar cells. Therefore, non-local models have been used following Baudrit&Algora procedures [BA10]. Baudrit&Algora applied the non-local models to GaAs/GaAs tunnel junctions. Here we apply those models to two different tunnel junctions used in multijunction solar cells, namely AlGaAs/GaInP and AlGaAs/GaAs. In order to include tunnel junctions into a multijunction modelling, calibration parameters for the non-local model have to be calculated. Additionally, the optical behaviour of such structures was compared to EQE measurements in order to validate the optical constants of the materials. The first tunnel junction corresponds to an AlGaAs/GaAs tunnel junction with barrier layers while the second one is an AlGaAs/GaInP p-n junction without barrier layers. Fig. 3.30 shows the data-fitting that is achieved for both cases.

Nevertheless, it should be mentioned that by introducing the nominal structure for the case of AlGaAs/GaInP TJ, no satisfactory data-fitting could be achieved. This structure has a very thin GaAs layer between anode and cathode and its practical role may have a strong impact on the

⁷Experimental data provided by E. Barrigón and I. García. Samples shown in this section correspond to annealed structures, i.e., samples have been subjected to an additional thermal load emulating the total growth of a multijunction structure. See more details in [GRA12a; Bar+14]

output. We speculate that a possible inter-diffusion of dopants or even a formation of a ternary or quaternary material between anode and cathode may be playing a key role. In fact, by assuming a low bandgap material (GaInAs with 20% of In composition) able to increase the tunnelling path and also to augment the contribution of trap-assisted tunneling permits an reasonable fit for the ohmic (0-0.1V) and excess current (0.4-0.6V) regions⁸ of Fig. 3.30. Assuming non-physical extremely low values of the effective masses allowed to fit the J_{peak} but not the whole curve. In any case, for multijunction purposes, both tunnel junctions considered are state-of-the-art devices capable to handle extremely high current densities, thus the voltage drop is almost negligible. Accordingly, when operating inside a multijunction structure and at very high light concentrations, it is expected that tunnel junctions will not be operating in the excess current region where trap assisted tunnelling dominates the curve.

Figure 3.30: Experimental and simulated I-V for the AlGaAs/GaAs (left) and AlGaAs/GaInP tunnel junction by using non-local tunnel junction models and trap-assisted tunnelling models.

The QE performance of the middle cell affected by the transparency of the tunnel junctions has been evaluated in order to test the optical constants. Simulations with and without antireflection coating were performed and compared to experimentally available data for both tunnel junctions (Fig. 3.31). Reasonable good agreement is achieved, despite the deviation at low wavelengths for the ARC-less structure of AlGaAs/GaAs TJ validating the simulation model. These simulated structures will be inserted into the multijunction solar cells studied in the following chapters.

⁸The negative differential resistance region exhibits time-dependent oscillations that increase the complexity of the measurements, thus data fitting.

Figure 3.31: Experimental and simulated EQE of Ga(In)As subcells (with and without ARC) with two different tunnel junctions. A GaInP layer of 750 nm acts as an optical filter [Bar+14].

3.6 Summary and conclusions

In this chapter, the validation of the models to GaInP, GaAs, Ge subcells and tunnel junctions has been carried out. Analysis of the GaInP subcell showed that the present structure is fully dominated by SRH losses. Besides, a breakdown of the main limiting layers has been presented allowing the assessment of the improvement of GaInP solar cells by increasing the bandgap and base thickness in multijunction solar cells. Assuming that Sb does not degrade the minority carrier properties of the material, the increase of the bandgap of the GaInP solar cell with the use of antimony was found to be beneficial.

The tunnel junctions were also validated with dark I-V curves as well as quantum efficiency. Calibrated parameters for two different structures were extracted for their use in multijunction solar cell devices.

In the case of GaAs and Ge subcells more extensive analyses have been carried out. The first part presented a 3D model for the perimeter recombination in GaAs diodes and solar cells. The model assumes the variation of the charge density at the perimeter surface by considering a given density of traps. Additionally, GaAs diodes on two epiwafers with different base doping levels, sizes and geometries, namely, square and circular, have been manufactured. An excellent fitting of the experimental dark IV curves of these diodes is used to validate the proposed model. By using the model, it is found that a surface channel region with a width of some tens of nanometers is proportional to the space charge density created by perimeter surface states. The model is able to explain why the perimeter recombination is dominant at low voltage biasing but it can be also very influencing at high biasing. Detailed 3-D figures of electrostatic poten-

tial and recombination rates are calculated for the real devices manufactured. An interesting result is the explanation of the influence of the bulk doping level on the perimeter recombination which is experimentally found in manufactured GaAs diodes. The 3D model is used to analyse the influence of doping level, size and geometry (square and circular) on the perimeter recombination affecting GaAs concentrator solar cells. As a result, it is found that small solar cells can be influenced by perimeter recombination even beyond the typical operation point of concentrator cells (about 1 V) and that square cells exhibit a lower perimeter recombination than circular ones. In any case, the control of the doping level can be used as one of the ways to decrease perimeter recombination. Finally, the model was also used under illuminated conditions achieving excellent fitting to the experimental data (dark and light I-V curves as a function of the light concentration) and providing the main key losses within the present structure.

Finally, a model has been developed for the germanium solar cell with special focus on the role of the emitter and interface between GaInP nucleation layer and emitter. An exhaustive validation of the model has been carried out for samples with different degree of degradation due to the thermal load associated to the growth of the top junctions as well as different properties of the base layer. It has been found that the potential barrier formed at the heterojunction (GaInP/Ge) due to the emitter graded profile was not able to explain the performance degradation of the solar cells. Instead, the most degraded solar cell (*etched* device with a loss of 60 mV) was explained by degrading severely one portion of the emitter layer practically acting as a *dead* layer. A sensitivity analysis of the minority carrier properties has been carried out for all samples. All the structures (*as-grown* and *etched* devices) were entirely dominated by the emitter and/or interface recombination at GaInP/Ge(emitter). Interestingly, the V_{oc} showed different slopes as a function of light concentration for the *etched* devices. V_{oc} started to recover when increasing the light concentration, thus approaching to the solar cell cases that did suffer less severe degradations. We speculated that a possible reason to explain this is the enhancement of the minority carrier lifetime as a function of the injection level (not considered in our model). This enhancement should be attributed to the emitter region close to the interface with the nucleation layer. Another hint may be a possible modification of the electrically active (or effective) carrier concentration may take place at higher light intensities. All in all, this behaviour is still under investigation.

CHAPTER 4

Simulation, characterization and analysis of GaInP/Ga(In)As/Ge 3J solar cells

4.1 Introduction

This chapter deals with the simulation, characterization and analysis of lattice matched GaInP:Sb/Ga(In)As/Ge 3J solar cells. First, a comprehensive fitting of the model to the experimental baseline structure is described together with an in-depth analysis by means of device simulations. Then, a couple of case studies targeting less studied applications is presented, namely the potential use of multijunction solar cells operating under ultra-high irradiance (>1000 suns), and the influence of proton irradiation on concentrator solar cells for space applications intended to operate under concentrated irradiance for near-sun missions.

4.2 Modelling and characterization of GaInP:Sb/Ga(In)As/Ge 3J solar cells

The lattice matched 3J GaInP/Ga(In)As/Ge solar cell is the most studied multijunction structure for PV applications. This is indeed the workhorse multijunction solar cell commercial product offered by companies (AZUR, Spectrolab, SolAero, CESI, among others) including space and terrestrial applications. It is a monolithic 2-terminal device grown lattice matched to Ge active substrates that offers simplicity and high efficiencies (41.6% at 400 suns terrestrial hold by Spectrolab and about 30% for space achieved by AZUR). Because it is the most studied structure, it is an excellent candidate to fully validate the modelling framework developed in this thesis. Despite the extensive literature available for this structure, the same literature is significantly scarcer regarding the modelling by using device simulators. Indeed, this is not only applicable to the GaInP/Ga(In)As/Ge 3J solar cell, but also to multijunction solar cells in general. Accordingly, here we will briefly describe some of the works regarding the use of numerical device simulators for multijunction solar cells.

Michael introduced back in 2005 the capabilities of Silvaco Atlas to deal with multijunction structures and local tunnel junction models. Then, the simulation of an inverted and lattice matched triple junction solar cells was carried out by using Crosslight APSYS software (see [Li+08; LXL07; LXL06] and references therein). At the same period, the inclusion of non-local models enabled more realistic simulations and their suitability for multijunction solar cells was demonstrated by Baudrit et al. (using Silvaco Atlas, see [BA08; BA10]) and Hermle et al. (using Sentaurus from Synopsis, see [Her+08; Phi+08]). Later, Olson et al. showed the potential use of these simulators on the detection of potential barriers affecting the FF of a solar cell operating under high irradiance [OSK11]. Additionally, by using the same software

(Crosslight APSYS), Olson studied the effect of non-uniform irradiance on multijunction solar cells [Ols10]. The study of multijunction solar cells was also carried out by simulating each subcell individually. For instance, Haas et al. proposed a design to maximize the energy yield of GaInP/GaAs dual junction solar cells by using ADEPT [Haa+11]. More recently, Walker et al. proposed a triple junction solar cell design including a chalcopyrite CuInSe₂ (as 1 eV material) based on device simulations [Wal+14] and Wilkins et al. presented a simulation of a full 4J solar cell including dilute nitrides in order to evaluate its potential for concentration applications and the capabilities of device simulators to deal with four junctions [Wil+13; Wil+16].

Although, there have been some excellent works showing the potential capabilities of numerical device simulators, these simulators are still in their validation phase for multijunction solar cells. While some of these works simulate structures without including tunnel junction models—simulating the individual behaviour of each subcell, then summing up their I-V curves—, some others do include TJ-models, but the comprehensive comparison of simulation results with experimental data is still pending. In general, less attention has been paid to the comparison between modelling and experimental results. This is where we focus most of the attention in order to validate the models used within this thesis, especially under different optical and voltage bias conditions. In addition, because of the complexity in the development and functionality of device simulators, it is always useful to show the output results of this type of simulators (especially from different software suppliers) for benchmarking. This will help increase the confidence on the results, analysis and material parameters extraction.

Accordingly, the main objective of the next section is to show how device simulations based on drift-diffusion and quantum models are now able to reproduce and *predict* the performance of multijunction devices. We will also mention their limitations and suggest pathways for improvement.

4.2.1 Model validation and analysis

A GaInP:Sb/Ga(In)As/Ge 3J structure is studied in detail and used to validate the multijunction solar cell modelling (see Fig. 4.1). An important difference from most commercial products concerns the top cell. Antimony has been incorporated into the ternary compound to disorder the crystal structure material aiming at bandgap increase. Antimony has only been incorporated into the base region while the emitter exhibits partial ordering, and thus shows lower bandgap. Details on the growth can be found elsewhere [Bar+09; Bar14]. Solar cells of 1 mm² were manufactured by conventional photolithography and wet-etching processes. The front metallization grid corresponds to an inverted square configuration with a shadowing factor of 2.7%. In some

cases (QE measurements with no ARC), a solar cell without any metal grid pattern (provided with a Ni pad front contact) has been used to avoid any influence of the metal fingers. Final devices include an anti-reflection coating deposited by thermal evaporation using a nominal $\text{MgF}_2(3\text{nm})/\text{ZnS}(50\text{nm})/\text{MgF}_2(100\text{nm})$ tri-layer.

Figure 4.1: (a) Nominal structural design of the GaInP/Ga(In)As/Ge triple junction analysed. (b) Band diagram in equilibrium conditions for the 3J solar cell. A MgF_2/ZnS anti-reflection coating of was deposited in some devices.

One of the main drawbacks in the use of physically-based simulators is the lack of reliable material parameters. In the case of multijunction solar cells the complexity rises since the devices have usually more than 20 semiconductor layers (as the case of 3 or more junctions). In addition, several III-V homo- and heterojunctions are formed through the whole multijunction solar cell (MJSC) structure and their properties and band offsets must be introduced into the simulator. Accordingly, reliable optical and electrical material parameters as well as models for the device performance must be used to ensure confident results. To validate the simulation environment for multijunction cells, we use previous knowledge described in Chapter 3 together with the comparison of the performance of the solar cell to conventional PV characterization such as: 1) dark I-V for the 3J device, 2) subcell I-V curves (extracted from EL measurements), 3) calibrated 1-sun light I-V curves, 4) EQE (and IQE) and 5) calibrated light concentration measurements.

Spectral electroluminescence was performed in order to calculate the internal voltages of

devices and have access to each specific subcell¹. This is calculated by following the reciprocity relation between electroluminescent emission and external quantum efficiency of solar cells [Rau07; Kir+08; Gei+14].

Moreover, we have fitted the calibrated light concentration measurements made at the certified calibration laboratory of FhG ISE of one of our solar cells with the nominal structure of figure 4.1. This has been done by using the same set of material parameters (most of them found in Appendix A and some others detailed later in this section) and models and changing the biasing conditions.

4.2.1.1 QE and Reflectance

Devices with and without ARC have been used to measure QE and R. The reason why we use devices with no ARC is mainly because an ARC greatly smooths the optical behavior of the semiconductor layers of the structure. Therefore, we first validate the optical constants, model and material parameters as well as the thickness and doping concentration of each layer by comparing EQE, IQE and R for devices without ARC. Then, devices including an ARC were used and calculations including its performance were carried out. Because final devices with an ARC include a metal grid pattern that could influence QE measurements, the subcell QE is multiplied by a corresponding scaling factor extracted from calibrated 1-sun multi source simulator. This allows to obtain absolute QE's which are of special importance in multijunction devices mainly because the QE measurement setup involves many sources of uncertainty (amplification and lock-in stages, spectral resolution of the monochromatic beam, influence of metal fingers, underfilling of the illumination area, different illuminated area, the need of voltage² and light biasing, etc.). Therefore, the comparison of simulation results to absolute QE measurements would enhance the accuracy of the material parameters extraction and models.

The experimental and simulated IQE, EQE and reflectance (specular) are shown in Figs. 4.2a and 4.2b for devices with and without ARC. In both cases, the agreement between ex-

¹EL measurements were performed at NREL facilities. Details on the setup can be found in section 6.3.2

²QE of multijunction solar cells is performed at short circuit conditions of the subcell to be measured. Nevertheless, in practice under a given spectrum, the subcell limiting the photocurrent is operating under reverse bias which is the sum of the open circuit voltages of the rest of the subcells. Therefore, if the QE of the limiting subcell has a non-zero slope at reverse bias (i.e. shunt effect), the J_{sc} under 1-sun or calculated from absolute QE curve may be inconsistent. This is another example that exhibits the complexity of measuring the *true* QE of a multijunction solar cell. Anyhow, for a III-V solar cell with high material quality such as the ones of the state of the art, the voltage dependence of the QE is very low or non-existent.

perimental and simulated values is quite good. The highest difference (highlighted by the J_{sc} deviation) does not exceed 1% in any subcell for both with and without ARC. In the case of the Ga(In)As subcell, typical oscillations related to a resonant cavity are observed. The phase shifting is perfectly simulated while the amplitudes show some discrepancy that can be attributed to a possible non-uniformities in thickness (GaInP base and/or BSF) and in a lower extent to a possibly partial coherence of light within thick layers of the subcell structure, i.e., the GaInP base. We speculate that this amplitude deviation is related to possible non-uniformities in thickness and/or measurement uncertainty rather than a possible second order effect in this case such as partial coherence of light. This is because of two reasons: 1) reflectance measurements are very sensitive to slight changes in layer thicknesses, thus small non-uniformities can be translated into significant measurement differences and 2) we have perfectly fitted these oscillations within the Ga(In)As absorption range in other 3J similar solar cells indicating that the formalism used here for photogeneration is valid. Indeed, those structures contain different GaInP base thicknesses —which is the main responsible parameter of the phase shifting— were the amplitude of the oscillations were matched. All in all, the J_{sc} difference is not larger than 0.5% supporting the use of the model.

It is also worth to mention the disagreement between experimental and simulated QE and R of the bottom subcell. Phase shifting and large amplitude deviations (in some cases as a consequence of the phase shifting) are detected in both cases: with and without ARC. This may be attributed, again, to oscillations associated to the resonant cavity existing in the the top layers (transparency in the Ge range as well as thicknesses of the order of incident wavelength) above the Ge subcell as well as error measurement uncertainty³. Possibly to a lower extent, fluctuations in light reflections can be observed due to the partial coherence length of light as mentioned previously. Let us remember that the present model considers that, each layer behaves coherently (and the substrate as a semi-infinite layer, see more details in section 3.4.1), but different scenarios may affect the partial coherence of light, namely: roughness at the surface or interfaces, the nature of light sources as well as possible thickness inhomogeneities. In this regard, no significant roughness is expected at the surface or interfaces of III-V epitaxial films grown here supporting the assumption of neglecting contributions from diffuse light in the model as well as in the measurements. Nevertheless, it should be mentioned that although its

³Many sources of uncertainty can appear in reflectance measurements performed along this thesis. Because we have used the same setup than the one used for QE (monochromator-based), all possible sources of error in conventional QE measurements apply to this kind of measurement. Moreover, if the sample has a metallization grid pattern, this can be very reflective thus influencing substantially the amount of reflected light.

Figure 4.2: Experimental (symbols) and simulated (lines) EQE, IQE and R for the GaInP/Ga(In)As/Ge 3J solar cell. Dashed lines indicate the QE contribution of each layer within the corresponding subcell. The numbers within brackets correspond to the J_{sc} of simulated curves while the numbers without brackets correspond to the experimental ones, both calculated using the AM1.5d ASTM-G173 spectrum.

impact is a second order effect —and only affecting the transparency region—, the back side of the Ge substrate is not typically polished (see for instance [Ari+17]) and some roughness can be found which may alter its optical behavior.

The inability to deal with partial coherence of light does not discredit the use of the present model, as only very low deviations from J_{sc} ($<2\%$) have been found. However, it may raise its importance when dealing with different devices or architectures. Indeed, as mentioned in previous sections, complete incoherence could play an important role on III-V multijunctions on Si where thick glasses ($\sim 600\mu\text{m}$) are used as handler and placed between the III-V tandem and Si solar cells (typically $>200\mu\text{m}$) [Ess+16]. Furthermore, sun light is partially-coherent by nature due to its finite coherent length and finite spectral width [Pre00]. In this sense, several methods have already been proposed to deal with partial coherence of light. Their suitability for device simulators — such as the one used here— remains however, unexplored [Pre00; KS02; Tro+10; Lee+12]. Although we speculate that the main cause of those deviations can be related mainly to small non-uniformities in thickness and the complexity/uncertainty in the measurement of absolute reflectance, we intend to evaluate the inclusion of partial coherence of light in order

to expand the capabilities of device simulators. Accordingly, even though the Transfer Matrix formalism used for these calculations does not deal with partial coherence/incoherence of light, the negligible deviations in photocurrent —well below the range of measurement error— back its applicability.

Regarding the electrical performance of the structure, the quantitative contribution of each region to the total QE is also shown in the top graph of Figs. 4.2a and 4.2b as depicted in Table 4.1. As expected, the SCR shows almost perfect collection efficiencies ($CE > 97\%$) in all cases. The GaInP subcell is the one that shows the highest collection efficiency for any layer disregarding the window layer. Interestingly, the emitter CE of the mid-subcell is about 80.1% when for single junction cases is above 90%. The emitter CE in Ga(In)As is lower than expected (compared to the single junction case reported back in Chapter 3 where the emitter $CE > 90\%$), being the main limiting layer since the base layer shows $CE = 98.8\%$. This suggests that the thinning/removal of the emitter would be beneficial for QE purposes. In fact, in order to achieve data fitting for Ga(In)As, significantly higher interface recombination velocities were assumed between window/emitter (about 1 order of magnitude higher than the single junction case). Germanium subcell is also limited, as expected, by the emitter+interface recombination at the nucleation/emitter (see section 3.4 for further details on how to enhance the emitter collection).

Table 4.1: QE contribution and collection efficiency for the main active regions of each subcell of the 3J solar cell. The contribution from the rest of the layers is negligible and is not shown for simplicity.

Subcell	Window		Emitter		SCR		Base	
	QE (%)	CE (%)	QE (%)	CE (%)	QE (%)	CE (%)	QE (%)	CE (%)
GaInP:Sb	1.5	6.2	55.8	87.4	31.7	97.9	10.9	84.3
Ga(In)As	0.05	97.5	5.3	80.1	37.4	99.8	57.2	98.8
Ge	0	-	9.2	70.4	11.2	99.9	79.5	79.8

4.2.1.2 Light, dark J-V curves and subcell internal voltages

Reasonable good agreement is also obtained by comparing light and dark J-V curves of each subcell (from EL measurements) and calculations together with the full 3J J-V curves (see Fig. 4.3a and 4.3b and Table 4.2). The ideality factors extracted are 1.25, 1.44 and 1 for GaInP, Ga(In)As and Ge, respectively. In the absence of SRH recombination (bulk and interface) indicated by dashed lines in Fig. 4.3a, germanium cell would get the highest benefit by increasing its V_{oc} by 77 mV. This corresponds to roughly one third of its total open circuit voltage. GaInP

gains about 12% (159 mV) while Ga(In)As shows the highest material quality among the three subcells with a gain of 54 mV (5.6%). If we look at the difference between solid and dashed lines in Fig. 4.3a, it can be seen that Ge shows the same slope at low and high voltages. This is not the case of GaInP:Sb and Ga(In)As. In particular, Ga(In)As is very affected by perimeter recombination at low voltages while at high voltages the simulated dark J-V approaches the one neglecting SRH losses. This is an indicator that at high voltages, radiative recombination dominates the performance of Ga(In)As. To a lower extent, GaInP:Sb also approaches at high voltages the dark curve without SRH losses, but the deviation is still significant. In this case it is not possible to assess in this manner that the device is purely radiative-dominant at high voltages. It should be mentioned that this assumption (no SRH losses) is not exactly the radiative limit. We are considering bandgap narrowing, real mobilities as well as the fundamental losses such as Auger and radiative recombination which are carrier concentration-dependent. Therefore, it is a more realistic assumption providing quantitative voltage losses in each subcell due to crystalline defects.

(a) Experimental (symbols) and simulated (including perimeter recombination) dark J-V curves of each subcell and the full 3J device. Dark J-V curves for cases neglecting SRH recombination are also depicted for each subcell (dashed lines) as well as from detailed balance calculations (d-b).

(b) Experimental 1-sun (AM1.5d ASTM-G173 spectrum) J-V curve for the 3J device (circles) and simulated J-V curves for each subcell and the 3J device (solid lines). The J-V curves including perimeter recombination are depicted (dashed lines).

Figure 4.3: Dark and light J-V curves for the 3J solar cell and its corresponding subcells.

GaInP is affected by voltage losses related to partial ordering effects. In section 3.3, we have shown that our single junction GaInP cells developed an open circuit voltage about 1.37 V which is ~ 50 mV higher than the one developed here (see Table 4.2). The single junction case has a partially ordered GaInP and the estimated bandgap is about 1.83V while the estimated bandgap in the GaInP:Sb is about 1.87-1.88 eV. Accordingly, recombination mechanisms ap-

Table 4.2: Experimental and simulated I-V parameters for the 3J solar cell and their corresponding subcells illuminated at 1-sun AM1.5d ASTM-G173 spectrum. The V_{oc} gain by neglecting SRH recombination losses is also depicted.

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	$\eta(\%)$	$\Delta V_{oc}, \tau_{SRH} \rightarrow \infty$ (mV)
3J - Exp.	14.40	2.489	0.852	29.91	-
3J - Sim.	14.38	2.513	0.830	29.99	258
GaInP	14.38	1.321	0.835	15.80	157
Ga(In)As	14.76	0.955	0.826	11.72	60
Ge	18.02	0.237	0.661	2.71	61

pear in GaInP:Sb contributing to V_{oc} degradation as it will be discussed later.

Ga(In)As shows a similar behaviour to the single junction explored previously. On the contrary, Ge exhibits a V_{oc} close to 240 mV which is about 60 mV higher than the ones studied in detailed in section 3.4. We speculate that these discrepancies between Ge studied in section 3.4 and this one are related to different quality of the wafers used in both cases that are not considered in the simulations. This is mainly because thermal loads are very similar in both cases.. Anyhow, this is still under investigation.

Finally, Fig. 4.4 visually summarizes the results of this validation process and shows a good agreement between experimental light concentration measurements and theoretical calculations. In this case a lumped series resistance has been included into the calculations following the procedure found in [AD00]. FF (thus the efficiency) exhibits the higher discrepancy. Typically, flash concentration measurements that use an unfiltered-Xe lamp may lead to an artificial increase in the efficiency of a multijunction solar cell due to an overestimation of the FF . The resulting uncertainty can be in the range of $\sim 4\%$ for concentrator Ga(In)As based cells and $\sim 1\%$ for Ge-based [Eme11; Ost+14a; Ost+14c]. In fact, an additional error to the intrinsic flash measurement uncertainty arises when the bottom cell is over illuminated. Accordingly, the discrepancy (lower than 2.5% absolute) between the calculated fill factor and the measured one shown in figure 4.4 can be justified. V_{oc} is probably the most reliable parameter to be compared in flash measurements because it is far less sensitive to photocurrent changes as well as current matching conditions than FF is. About 15-30mV deviations (mostly attributed to Ge) have been detected corresponding to a relative difference $\sim 1\%$ for the highest deviation. In this sense, we have also depicted the results from EL measurements (violet empty circles) to confirm that no significant voltage overestimation took place because of the use of HIPSS

rather than T-HIPSS measurement technique as stated in [Ost+14b].

Figure 4.4: Solar cell parameters of calibrated concentration measurements of a GaInP/Ga(In)As/Ge triple junction solar cell. The baseline structure has a measured peak efficiency of 39.2% at 400 suns and about 37% at 1000 suns

4.2.2 Layer-by-layer recombination losses under dark conditions

Getting experimental access to internal subcell voltages by different techniques (i.e. Fig. 4.3a) is a very powerful and useful way to analyze the individual behaviour of each subcell in a multijunction stack (see for instance [Kir+08; Nes+15]). Nevertheless, it is not easy to have access to the layer-by-layer behaviour of each subcell. In this regard, device simulations are able to provide several outputs such as band energy diagrams, carrier concentrations, generation and recombination losses as a function of depth or in a layer-by-layer basis. Together with a proper model validation, these output can be very useful in providing more insight into the fundamental operation and the limiting regions or mechanisms. Indeed, this is one important advantage of using device simulations in order to asses enhancements of a given structure. Fig. 4.5 shows the recombination current by regions and types for Ga(In)As and Ge, while GaInP:Sb will be described later.

In the case of Ga(In)As, the results obtained indicate that the base entirely dominates the dark current, being SRH recombination the main dominant mechanisms at voltages below 1V as can be seen in Fig. 4.5. Radiative recombination contributes about 20% at 1V while the crossover between SRH and radiative recombination occurs at 1.21V. At 1.3V where radiative recombination reaches 70% of the total. This is consistent with previous analysis on Ga(In)As

subcells presented in sections 3.2. Germanium exhibits similar contribution from the emitter (including interface recombination between the nucleation layer and emitter, IR_{WE}) and base at any voltage analysed.

Figure 4.5: Top graph: recombination current density at different regions for: Ga(In)As (left) and Ge (right) as a function of voltage bias. Black dashed horizontal line indicates the current value matching the J_{sc} of this multijunction solar cell at 1-sun. Middle graph: recombination by types (radiative and non radiative) for the dominant layers, namely emitter+ IR_{WE} (E) and base (B). Bottom graph: fraction of total recombination occurred at base (red) and emitter+ IR_{WE} (green) as a function of voltage bias.

The case of GaInP deserves special attention. The dark J-V curve cannot be explained by just one dominant region, as the case of Ge and Ga(In)As (including perimeter recombination)⁴. If only one of the layers (emitter or base) dominates the recombination, the simulated curve fits well either at low or at high voltages, as can be seen in Figs. 4.6a and 4.6b, but not over the whole curve. Therefore, the experimental J-V curve must be explained by a combination of base and emitter recombination currents.

⁴For Ga(In)As, it is not expected that the emitter may severely impact the dark J-V curve, as in the case of GaInP:Sb. We have shown that the base contributes above 80% up to 1.2V bias, being radiative recombination a very important mechanism at voltages above 1V. Thus, if the emitter is very poor it would substantially affect the performance at high voltages. Moreover, our GaAs develops a V_{oc} similar to the single junction case indicating that dominant base is consistent. In the case of germanium, there is no significant flexibility in the minority carrier properties assumed at the emitter in order to fit the data. Accordingly, no sensitivity analysis has been performed on these subcells.

(a) Dark recombination current dominated by the base region. (b) Dark recombination current dominated by the emitter region.

Figure 4.6: Experimental (symbols) and simulated (lines) dark J-V curves of GaInP:Sb subcell for different values of minority carrier lifetimes: base (left) and emitter (right).

The recombination currents extracted and shown in Fig. 4.5 are very sensitive to the minority carrier properties. Our typical methodology is to fix the minority carrier mobility (when available) and vary the minority carrier lifetime to match the experimental results. This is because carrier mobility is less sensitive to growth conditions (i.e., temperature, V/III ratio, flow rate, etc.) while carrier lifetime is strongly dependent on them, which impacts the growth technology quality. Minority carrier lifetimes for germanium and GaAs are available in the literature, however, this is not applicable to GaInP:Sb mainly because minority carrier properties for both emitter and base in GaInP:Sb⁵ are not known and they are very dependent on growth conditions. Thus, it is not possible to fix the mobility. It is also likely that the introduction of surfactants such as Sb affects the conductivity, native defects and mobility in GaInP [Str02]. Furthermore, anisotropy of minority carrier mobility has been detected from direct transport imaging techniques that could affect diffusion length [Hae+14] of carriers. Consequently, there is a high degree of complexity in knowing the minority carrier properties of a given GaInP that require extensive experimental work⁶. In order to overcome the lack of information and the material parameters dilemma, we have decided to perform a sensitivity analysis of the main

⁵Minority carrier mobilities for several doping concentrations have been recently deduced from measurements of carrier lifetimes and diffusion length for p-type MBE-grown samples in [Hae+14]

⁶Typically, minority carrier mobility experimental determination is done by obtaining the minority carrier lifetime using TRPL and the diffusion length by EBIC, transport imaging techniques, among others (see [Sch+13; Hae+14; Nie+17]). Then, from these two parameters (diffusion length and minority carrier lifetime), minority carrier mobility is calculated straightforwardly by the Einstein relation.

material parameters involved. This allow us to establish upper and lower bounds — that fit accurately the QE and dark J-V— in the distribution of recombination losses by layers. The sensitivity analysis is based on the following procedure:

1. Emitter and base diffusion lengths are extracted from QE data fitting.
2. Dark J-V curves as a function of $\tau_{h,E}$ and $\tau_{e,B}$ are computed by using the same diffusion length to keep consistency with QE data fitting, i.e. the minority carrier mobility is calculated from the minority carrier lifetime swept by using: $L_D^2/\tau_{SRH}kT$ (See footnote ⁷).
3. Extract the range of parameters where V_{oc} is matched within a reasonable tolerance (± 5 mV).

Three set of parameters were extracted with the following characteristics. The first set we call *best emitter* case using the following minority carrier lifetime ratio between base and emitter: $\tau_{e,B}/\tau_{h,E} = 14.3$. The second set is called *best fit* and $\tau_{e,B}/\tau_{h,E} = 21.8$; and finally the third set is called *best base* with $\tau_{e,B}/\tau_{h,E} = 50$. Any minority carrier lifetime ratio lower than 14.3 and above 50 deviates by more than 5mV in any J,V data point of the dark curve. The range of carrier mobilities deduced for holes at the emitter is 346-660 cm²/V·s and 470-826 cm²/V·s for electrons at the base. The range of values for electron mobility in p-type materials is indeed consistent with [Hae+14] while no data is found in literature for holes in n-type GaInP materials.

Fig. 4.7 shows the recombination current for GaInP:Sb subcell as a function of voltage bias. For all cases, the total recombination is a combination of emitter (although low, it includes IR_{WE}) and base contributions. For all cases, SRH recombination strongly dominates the recombination current. The contribution of radiative recombination is lower than 1% even at voltages up to 1.55V. At this level, the operating point of the cell can be associated to the performance at about 1000 suns. Therefore, even at 1000 suns the cell is strongly dominated by SRH recombination. As can be seen in the bottom graphs, the base dominates the performance at low voltages while the emitter increases its influence at high voltages. Different crossovers are detected depending on the set of parameters used, shifting within a range of 100mV. Specifically, the crossover points are 1.41V, 1.37V and 1.31V for the *best emitter*, *best fit* and *best base* cases. Indeed, the voltage window for a reasonable good fit is rather large (100mV). This

⁷This approach is only valid as long as the QE does not significantly change independently of the μ/τ ratio.

indicates the high sensitivity of the dark J-V curve to the recombination processes occurring within the device. In fact, it is not clear up to which extent each layer dominates, specially at low voltages. In the lower bound (*best emitter* case) the base and emitter contributions are about 70% and 30% at 1-sun while at the upper bound (*best base* case) is about 50-50. The *best fit* case indicates that at that irradiance level, the contributions are 65% and 35% for base and emitter, respectively. At high voltages (above 1.41V), it is clear that the emitter starts to dominate the performance.

We now come back to the V_{oc} degradation with respect to the single junction cases of GaInP:Sb subcell. Poorer minority carrier properties or different doping concentrations modified by the presence of Sb can be some of the causes. Indeed, the presence of Sb has strong implications on the growth of GaInP. On the one hand, Sb enhances Zn incorporation, thus doping concentration in the p-type base (see [OMK07; Bar+15b] and references therein), which could affect the minority carrier properties. Nevertheless, to compensate the Zn incorporation enhancement, careful calibrations were carried out and doping concentrations about 10^{17} cm^{-3} have been measured by ECV. This is the standard value used in previous single junction samples of Chapter 3 where a higher V_{oc} has been measured. Therefore, a possible difference in total doping concentration is ruled out. On the other hand, it has also been reported that electron lifetime decreases by increasing Sb [Fet+02; OMK07]. According to our simulations, some degradation of minority carrier properties is present at the base (the minority carrier lifetimes extracted is about 5 times lower than the case without Sb described in section 3.3), however, it seems that is not the sole cause behind the lower V_{oc} . In fact, we have already shown here that a strong mix of emitter and base contributions suggest that the emitter is also playing a role in the dominant recombination mechanisms. Another possible reason for the degradation of GaInP (either emitter or base), is the Ge autodoping that takes place during the growth of triple junction solar cells (see [Bar+17] and L. Barrutia PhD thesis [Bar17]). Although the carrier concentration measured was the targeted value, it does not necessarily means that Ge autodoping is not degrading the material quality.

4.2.3 Layer-by-layer recombination losses under light conditions

Typically, the analysis under dark conditions is easier and faster than under light conditions because several illumination steps should be performed involving higher complexity in the calculations and numerical convergence. As a consequence, time consuming and carefully designed simulations are required, especially if a rigorous model of tunnel junctions such as the non-local

Figure 4.7: Top graph: recombination current density at different regions of GaInP:Sb as a function of voltage bias for three different cases: *best emitter* (a), *best fit* (b) and *best base* (c). Black dashed horizontal line indicates the current value that match the J_{sc} of this multijunction solar cell at 1-sun. Middle graph: radiative and non radiative recombination for the dominant layers, namely emitter+ IR_{WE} (E) and base (B). Bottom graph: fraction of total recombination occurred at base and emitter+ IR_{WE} as a function of voltage bias.

band to band and local or non-local trap assisted tunneling models are considered⁸. Simulations can be assumed in 2D for the structures used here. In this regard, the simulation under dark and illuminated conditions can provide relevant information about the device physics. Indeed, the operation of the solar cell might not be the same under dark and illuminated conditions, including opposite current flow directions — where band discontinuities may play an important role depending on the design— and carrier concentrations are modified differently upon illumination. Accordingly, we have also computed the J_{sc} vs V_{oc} pairs as a function of light concentration and compared these curves to the dark ones. For GaInP:Sb (*best fit* case), the fraction of recombination is slightly different for both emitter and base and there is also some constant contribution coming from the window layer ($\sim 5\%$), undetectable from dark simulations. As can be seen, the difference between dark and illuminated behavior is voltage-dependent. At low voltages (to the left of the crossover point between base and emitter), differences up to 10% are observed while at higher voltages this is diminished to about 5%. The illuminated curve of the emitter (+ IR_{WE}) is above the dark one ($\sim 4\%$) at low voltages while at high voltages is slightly below ($\sim 4\%$). For the base, it is always below the dark one, thus this layer balances the

⁸By including tunneling models the simulation time increases by a factor of 4 for an appropriate tunneling mesh and for a specific set of models used in this thesis.

recombination. This is an interesting result indicating that although both sets of curves (J_{sc} vs V_{oc} and dark ones) develop virtually the same J-V curve, the contribution by regions is distinct. The cases of Ga(In)As and Ge are similar. The emitter recombination is higher under light than under dark conditions for both subcells, being almost constant with voltage. On the contrary, base recombination is higher at dark conditions for both subcells.

Figure 4.8: Fraction of recombination under dark (solid) and illuminated (dashed) conditions by regions of each subcell: GaInP:Sb (left), Ga(In)As (middle) and Ge (right).

Physically, minority carrier population at the window is increased by several orders of magnitude due to the illumination, thus so is the recombination rate. This is observed in Fig. 4.9. The recombination rate shows strong correlation with the hole concentration increase at the window due to the quasi-Fermi level splitting upon illumination (dashed lines). This unbalances the carrier concentration at the window and emitter interface, favouring interface recombination between these layers which explains the higher recombination at the emitter ($+IR_{WE}$) under illumination at low voltages. In other words, electron-hole pairs generated at the window recombine at this layer but also at the vicinity of the emitter. At high voltages, series resistance influences the recombination distribution at the emitter and base ($>1.4V$). Then, the base recombination should be balanced according to the overall recombination. For Ga(In)As and Ge, there is also a high increase in minority carrier concentration at the window and the vicinity of the interface window/emitter. Although window layers of these subcells receive less photons (already filtered by upper subcells), the emitter does receive a high amount and although small, the photogeneration at the window is not negligible, modifying substantially the hole concentration at that layer. Indeed, generation-recombination equilibrium at the window breaks because of the small injected fraction coming from the upper layer (i.e., Ga(In)As overbuffer layer) and non-negligible light absorption ($\sim 10^9 \text{ cm}^{-3} \cdot \text{s}^{-1}$), resulting in a hole concentration increase of several orders of magnitude from dark ($\sim 10^{-5} \text{ cm}^{-3}$) to illuminated conditions ($\sim 10^4 \text{ cm}^{-3}$).

The uneven recombination by regions under dark and light conditions is attributed to the impact of the window layer or/and the interface recombination. For instance, by neglecting

Figure 4.9: Recombination rate and hole concentration at ~ 1 -sun as a function of the depth within the GaInP:Sb subcell (left), Ga(In)As (middle) and Ge (right). The cross section is taken at 1/3 of the total length (illuminated area) of Fig. 4.1.

interface recombination in these subcells, the fraction of recombination in each region is equal in both dark and illuminated conditions. For GaInP:Sb, the same difference between dark and illuminated conditions is still observed because of the high photogeneration rate at the window.

The implications of different contributions under dark and illuminated conditions may have a major impact on devices with high recombination via interfaces. This is not the case analysed here (except Ge). Nevertheless, it should be mentioned that as devices approach to the Shockley-Queisser limit with very high bulk material quality, the relative importance of other recombination mechanisms such as interface recombinations (although low) might start to be relevant for improved device performance.

To evaluate the impact of the emitter+ IR_{WE} in all subcells, simulations were repeated by considering the absence of emitter bulk traps and interface states at the window/emitter interfaces. The V_{oc} increases at 1-sun by 21mV for GaInP:Sb and 32mV at 1000 suns. Due to this low increase, the lower than expected V_{oc} measured in this subcell cannot only be attributed to the emitter (at least in the low voltage range), consistent with the fact that both emitter and base are contributing similarly in the medium voltage range (1.3-1.45V).

Ga(In)As enhancement assuming a perfect emitter is negligible at low voltages (mainly due to perimeter recombination). At 1000 suns the increase is < 5 mV because base radiative recombination dominates.

Ge shows a constant increase in V_{oc} of 36 mV disregarding the light concentration which is consistent with the kT -behavior of its dark current independently of the limiting region.

Accordingly, if the emitter is redesigned or removed, some gain can be achieved and the device will become base-limited. It should be mentioned that it is difficult to evaluate the material quality of the device having an emitter, base or interface recombination limited device. In cases where photon recycling is not fully exploited (as is our case), a base-limited device may

be preferable because this will be an indicator that no other regions exceed the recombination of the thickest layer. Nevertheless, as devices approach to the S-Q limit some other relative contributions coming from the emitter or interface recombinations (albeit low) can indeed start to dominate the recombination losses mainly because the base recombination is so low that is comparable to such other low losses. Therefore, the examination shown here is very useful to elucidate which layers are presently limiting the device.

In summary, we can conclude that our simulation environment (model, material parameters, etc.) is suitable to reproduce the experimental performance of concentrator MJSC. It is also a very powerful tool for understanding the main limiting mechanisms in order to assess the improvement of devices. The model developed will be used to analyze the performance of MJSCs under different scenarios as it will be shown in the following sections.

4.3 Case study 1: Limiting factors of the semiconductor structure for Ultra-High Concentration (1000-5000 suns)

Multijunction solar cells (MJSC) designed to work under ultra-high concentration (>1000 suns) could be one of the ways to further reduce the cost of concentrator photovoltaic (CPV) systems [Alg07]. The operation at ultra-high concentration (UHCPV) is not only interesting in terms of cost reduction, but its understanding is also interesting for a better operation of the cell under high localized irradiances caused by most optical concentrators. Nowadays, remarkable advances on the performance of systems working above 1000 suns have been achieved, with module efficiencies exceeding 35% at standard test conditions [Gho+14]. Furthermore, new characterization techniques have been successfully developed showing the feasibility of testing the cells under ultra-high irradiances (up to 10,000 suns) [Kor+07]. Despite these recent advances, the potential of ultra-high concentration has not been fully explored in CPV. The main constraints include the performance of the optics used [Ben+10b; Her+12], the extraction of heat [Gho+14; Alg+06], and the behaviour of the cell.

Regarding solar cell performance, series resistance losses are one of the most important drawbacks of ultra-high concentration. The main components of series resistance (R_s) typically found in a well optimised multijunction structure are listed from high to low contribution as follows: a) top cell window and emitter (roughly half of the total), b) metallization grid and front contact resistance (roughly one third of the total), c) tunnel junctions (up to ten percent) and d) the potential barriers formed at heterojunctions (this may dominate the R_s depending on the heterojunctions present in the multijunction structure). It is important to mention that

the relative contributions to R_s are very dependent on technology and multijunction solar cell design. Different emitter and window properties may be used as well as different metallization grid, tunnel junctions or heterojunctions which may substantially unbalance the numbers given above. Whereas the contributions of the front metal grid [Alg07; Nis+06] and tunnel junctions [GRA12b; Bar+14] to the whole series resistance have already been thoroughly addressed for UHCPV applications showing their suitability, the other contributions related to the top cell and heterojunctions have not been fully explored. Both top cell window and emitter layers need to handle large current densities (they act as lateral current spreading layers). In the case of the contact layer, it is usually highly doped to achieve a good ohmic contact, and thus its electrical conductivity is assumed to be high enough⁹. In the case of heterojunctions, the potential have been shown to become very relevant under high irradiance, thus care must be taken when selecting the heterojunction systems to be used [Gal+06; KOM10; OSK11].

Accordingly, in this section we optimize the performance of lattice-matched GaInP/Ga(In)As/Ge triple junction solar cells under UHCPV by using the TCAD tool and models developed in this thesis. The optimization of the MJSC semiconductor structure has focused on the structural properties (thicknesses and doping levels) of the top emitter and window layers as well as on the role of heterojunctions inside the MJSC, since we have detected that the rest of layers do not significantly contribute to series resistance. Although this study is focused on the standard GaInP/Ga(In)As/Ge triple junction solar cell, the results can be applied to a large extent to other MJSC architectures such as inverted metamorphic, wafer bonded, diluted nitrides, etc. [Fra+15; Dim+14; SYW12].

Because of the key role played by the top layers of the GaInP top cell (i.e., window and emitter layers), material parameters such as carrier mobilities and lifetimes as a function of the doping level must be provided for the semiconductors constituting those layers, namely AlInP and GaInP (see figure 4.1). Accordingly, further details about these two materials are given in next subsections while all the other general parameters regarding all materials involved in the MJSC structure are given in the Appendix.

⁹The role of the contact layer has been detected to be negligible if high enough doping concentration is achieved ($> 10^{19} \text{ cm}^{-3}$). Nevertheless, most of the current crowding occurs within this layer and its role will be also dependent on the metal grid design. Furthermore, typical etching processes reduce the electrical contact area [Pra01a] (neglected in our case) being the contact width lower than the metal finger width, thus reducing its capability to drain current. Therefore, the role of the contact layer taking all previous statements into consideration has not been completely tackled in this section while we understand that optimizing the solar cell processing and shadowing factor are key aspects to counteract or completely mitigate its effects.

4.3.1 Methodology to assess the optimum design of multijunction solar cells for UHCPV

In this section, solar cells of 1 mm^2 are analysed due to the fact that: 1) the heat extraction at UHCPV requires the use of very small devices (about 1 mm^2 or smaller) since the heat dissipation is much more efficient [Gho+14; Alg+06]; and 2) small size solar cells also benefit from a reduction in the metallization grid losses. In fact, the approach followed here would only be affected in terms of metallization grid losses if different solar cell sizes were analysed. Although perimeter recombination increases in small solar cells (especially in GaAs [Esp+15b]), its impact is not a limiting factor at high concentrations as shown previously (see also [Fid+14]). All simulations were performed at 25°C due to the fact that heat extraction (and then, temperature) is strongly dependent on the thermal management strategy offered by the CPV module [GVA16a] and the lack of material parameters at high temperatures for the modelling to be accurate (i.e. electron and hole effective masses, conduction and valence band offsets, diffusion length of carriers, among others). Nevertheless, it should be mentioned that going to higher light concentrations raises the cell temperature, degrading the overall performance of the concentrator solar cell. The most affected parameter is the V_{oc} while the FF is the less affected one [GVA16a]. We analyse different R_s components. Since the FF is the most affected by R_s , it can be concluded that the overall impact of R_s under higher temperatures would be lower than the changes in J_{sc} and V_{oc} . Moreover, the solar cell parameters may reduce their sensitivity to temperature with concentration [GVA16a]. Accordingly, the main conclusions and general trends we achieve are not compromised by simulating at 25°C . This is also supported by the fact that for a well optimized grid, the larger contribution to R_s comes from the top cell window and emitter whose conductivity is expected to increase with temperature thus counterbalancing the resistivity increase from the grid with temperature. In the case of tunnel junctions, their contribution to R_s do not vary negatively at higher temperatures [Bar+14; Whe+09], while R_s from heterojunctions involves higher complexity to be quantified.

Regarding the semiconductor structure, both the top cell window and emitter layers were examined individually rather than, as an ensemble of both layers. First, the top cell emitter is evaluated at 5,000 suns to detect if the present emitter properties and the whole structure are suitable (i.e. $\eta > 40\%$) to work at irradiances from 1,000 to 10,000 suns. Then, the doping level and thickness of the emitter are optimized before proceeding to any further modification in the rest of the solar cell. After the emitter optimization, the conductivity properties of the top cell window layer as a function of doping level and light concentration are examined. The top

cell window layer is fixed to a value of 25 nm. Thinner layers would be desirable in terms of minimizing the absorption of high energy photons; however, they may compromise the emitter passivation quality [Gar10]. On the contrary, thicker window layers are undesirable because of the higher absorption of light. Therefore, the selected value of 25 nm results from a trade-off between good passivation properties and low absorption of light [Gar10]. Then, the recombination losses and high injection effects at high irradiance are discussed and examined. Next, the impact of heterojunctions is analysed at ultra-high concentration (5,000 suns) to detect which potential barriers formed can limit the performance. Finally, an optimization loop is carried out for the whole solar cell taking into account the preliminary optimizations from previous stages, following the criterion of maximum efficiency as a function of concentration.

4.3.2 Influence of top cell emitter

Fig. 4.10 shows a contour plot of the MJSC performance figures of merit as a function of the top cell emitter doping density and thickness at 5,000 suns. The best efficiency values are found for thin emitters (below 100 nm) and relatively high doping levels ($5 \cdot 10^{18}$ - $3 \cdot 10^{19} \text{ cm}^{-3}$). It is noticeable that the efficiency is mainly dominated by the short circuit current and the fill factor. The short circuit current drops with increasing emitter doping due to the worse minority carrier properties and the thickness of the emitter becomes more important when the doping level degrades the diffusion length up to a point (lower than $70\text{-}72 \text{ A/cm}^2$), where carriers cannot be collected efficiently. As a consequence, thinner emitters (below 50 nm) are required to maintain high efficiencies if the doping density increases above $3 \cdot 10^{19} \text{ cm}^{-3}$. It is important to mention that for thicknesses below 50 nm, the efficiency is high, but not the highest, being lower than the 42% peak corresponding to the white cross mark of Fig. 4.10. In other words, the efficiency starts to drop slightly for highly doped emitters with thicknesses below 50 nm (barely noticeable to the right of the white cross mark) because the overall light absorption is reduced and interface recombination becomes more significant. On the other hand, going to higher doping levels enhances the FF (stronger impact than thickness) as expected, due to better lateral conductivity. Therefore, the peak efficiency is 42% at 5,000 suns for a 50 nm emitter doped as high as $1.5 \cdot 10^{19} \text{ cm}^{-3}$ which is actually a trade-off between short circuit current and FF losses as usual in concentrator solar cell design.

Figure 4.10: Solar cell parameters of calibrated concentration measurements of a GaInP/Ga(In)As/Ge triple junction solar cell. The baseline structure has a measured peak efficiency of 39.2% at 400 suns and about 37% at 1000 suns.

4.3.3 Influence of the top cell window

The electrical properties of the window layer become more important as the irradiance is increased. This can be seen in the contour plot of Fig. 4.11. For concentration levels below 700 suns, the efficiency is not affected by the top cell window doping density. However, above this concentration, an efficiency gain up to 1% absolute (at 3,000 suns) can be achieved by increasing the doping level. Moreover, the peak efficiency is slightly shifted towards high irradiances, from 2,000 to 3,000 suns when the doping is augmented as indicated by the black dashed arrow. This gain is entirely related to a better performance in terms of FF because the changes in J_{sc} and V_{oc} are not significant.

The reason for the FF improvement is shown in Fig. 4.12 where the total current density at 5,000 suns through both the top cell emitter and window layers is depicted for two different top cell window doping densities. The total current density through the top cell window is significantly lower when the doping density is 10^{18} cm^{-3} (see Fig. 4.12a). For a higher doping density (10^{19} cm^{-3} , Fig. 4.12b), the current is able to spread through the window layer relieving the emitter layer from high current densities. Hence, the window layer may not be only a

Figure 4.11: Contour plot of efficiency as a function of the top cell doping density and concentration. The top cell emitter doping is $5 \cdot 10^{18} \text{ cm}^{-3}$ and the thickness is 175 nm.

passivation layer or hole minority barrier, but it also helps distribute the high current density from the emitter to the front contacts.

The efficiency gain observed in Fig. 4.11 may be reduced when the doping level of the emitter layer is increased (as suggested by Fig. 4.10) which would eventually enhance the conductivity of this layer. If the optimum emitter thickness and doping level values (50 nm and 10^{19} cm^{-3} values from Fig. 4.10) are used, the efficiency gain reduces to 0.8% which is still a significant increase. Therefore, the use of very high doping levels for the window layer enhances the performance of multijunction solar cells operating at ultra-high irradiance. A good lateral conductance at the window and emitter layers is also beneficial because a higher grid spacing may be used reducing the shadowing factor of the metallization grid.

On the other hand, it could be argued that AlInP mobility values are not well known for the doping range from 10^{19} to 10^{20} cm^{-3} . For example, from Eq. A.3 (see Appendix A), the calculated mobility for an AlInP layer with a doping level of 10^{20} cm^{-3} is $25 \text{ cm}^2/\text{V}\cdot\text{s}$ (see Appendix A, Fig. A.8). Since the mobility at such a high doping level is unknown, we have forced the case of a very poor mobility ($1 \text{ cm}^2/\text{V}\cdot\text{s}$) at the AlInP window layer. As a result of the calculation, the difference in efficiency is 1%, being obviously lower for the low mobility case ($1 \text{ cm}^2/\text{V}\cdot\text{s}$) than the nominal mobility case ($25 \text{ cm}^2/\text{V}\cdot\text{s}$). This efficiency drop is comparable to the relative efficiency drop calculated by fixing the mobility to $1 \text{ cm}^2/\text{V}\cdot\text{s}$ and increasing the doping densities two orders of magnitude (from 10^{18} cm^{-3} to 10^{20} cm^{-3}). Accordingly, assuming good metallization properties (as the ones stated previously), the effect of an *artificial* extremely low mobility on efficiency would be counterbalanced by using very

Figure 4.12: Cross-sectional color map of current density at maximum power point (~ 3 V) and 5000 suns of top layers in the GaInP subcell for two window doping densities (a) 10^{18} cm⁻³ and (b) 10^{19} cm⁻³.

highly doped window layers.

Typical concentrator cells operating around 500 suns have no requirements of higher top cell window doping levels (see Fig. 4.11); however, working at higher current densities would require doping levels higher than the one shown in Fig. 4.1. Increasing the electrical doping level (above 10^{18} cm⁻³) in AlInP is not an easy task to accomplish. Silicon-doped AlInP has been reported to reach doping levels around 10^{18} cm⁻³. Nevertheless, further increase of the doping level by using silicon is difficult because of the incorporation of aluminium and the occupation of Silicon in lattice sites of group III and V [Dai+15]. Anyhow, higher n-type doping levels can be achieved by using Se or Te dopants. In fact, we have measured doping levels of $2\text{--}3 \cdot 10^{19}$ cm⁻³ in Te-doped AlInP when the nominal values were 10^{20} cm⁻³ indicating that achieving very high doping levels is not straightforward. As far as we know, electrical doping concentrations up to 10^{19} cm⁻³ using Te is the highest electrical doping level reported [Dai+15]. It is also important to mention that very high doping levels may impact the intrinsic properties of the material and its related heterointerfaces. The use of very high doping levels may give rise to typical phenomena observed in III-V semiconductor alloys such as: a) band gap narrowing/widening affecting among others, the transparency of the window layer, b) the modification in the ordering degree of the material and c) the variation of the band offsets with the surrounding materials. Besides, deep level defects can increase significantly for very high doping levels. Although these issues may affect the performance, the suitability on the use of very highly doped AlInP windows in solar cells (up to 10^{19} cm⁻³ using Te) has been already

reported [Dai+15]. In summary, modelling shows that very high doping levels at the window layer enhance the maximum power point of the cells. In order to reach the high doping levels of 10^{20} cm^{-3} , the use of Se and Te as dopants is recommended. However, such a high doping level needs to be achieved and evaluated experimentally.

4.3.4 Recombination losses

We have examined high injection effects and different recombination mechanisms at a concentration level of 5,000 suns. Since high injection effects can be stronger in localized regions, they have been analysed where the maximum current density is found in the structure (i.e. under the edge of the front metal fingers at maximum power point, see Fig. 4.12). High injection effects are expected with higher probability at the active regions where most of the photo generation of carriers takes place. Specifically, the base region is likely to have an excess of minority carriers exceeding the doping level rather than the emitter due to the lower base doping level. As a result of the numerical calculation, we have found that the majority to minority carrier ratio is 2.7, 3.84 and 47 for top, middle and bottom cells, respectively. Hence, there are no clear signs of high injection effects in MJSC at 5,000 suns. Another possible limiting process of the solar cell efficiency under ultra-high irradiance is the impact of different recombination types. Auger recombination can be especially important because it increases as the cube of carrier concentration (see Appendix A). Moreover, in the present design, Auger recombination affects more Ge than GaInP or GaAs, since Ge has a lower-indirect band gap. In order to elucidate the impact and contribution of the different recombination mechanisms, we have analysed them under open circuit conditions where all generated carriers are lost by recombination. Shockley-Read-Hall (SRH), radiative and Auger recombination contributions can be seen in Fig. 4.13. It is clearly seen how SRH losses dominate mainly in GaInP and Ge subcells while radiative recombination is the main loss mechanism in the GaAs subcell. In this cases, improved modelling is achieved if photon recycling is considered self-consistently. Regarding Auger recombination (and excluding its role in tunnel junctions), it shows its largest contribution in the Ge subcell emitter (almost 50%), whilst it only reaches 8% in the Ge subcell base. Accordingly, we found no clear evidence of Auger-limiting processes at ultra-high irradiance by using the models described in previous section. This finding is supported by previous work developed by Vossier et al. showing that Auger-limiting behaviour from the Ge subcell does not show significant degradation in performance for concentration fluxes of thousands of suns [VHG10].

Figure 4.13: Fraction of different recombination losses within the multijunction solar cells (cross-section view) at 5000 suns. The recombination losses are calculated at open circuit. Please note that in order to show this plot clearly, the depth in the structure is not scaled and does not correspond to the real thickness of the layers.

4.3.5 Influence of heterojunctions

We found no significant limitations from the band discontinuities formed in any heterojunction (see Table 4.3) when they operate at very high irradiances (3,000-5,000 suns).

The interfaces between arsenides (e.g. AlGaAs/GaAs system) are well-known and their band offsets have been extensively studied. The case of the (Al)GaInP/GaAs system has been extensively studied too. However, the band alignment has been proved to be dependent on the ordering parameter of the phosphide and/or aluminium content when employed [Ada09]. Moreover, the band offsets are very dependent on the interface formed and the properties of the surface which are also dependent on the growth conditions. Consequently, it is reasonable to expect different properties at each heterojunction that need to be empirically determined. Nevertheless, we evaluate here as a case study the $(\text{Al}_{0.2}\text{Ga}_{0.8})_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ heterojunction formed between the top cell BSF layer and the anode of the high band gap tunnel junction. The reason why we chose this heterointerface is because to our knowledge there is no experimental data of the band offsets available in the literature. Anyhow, the analysis carried out here can be applied to any heterojunction with similar band alignments. Accordingly, we compare two cases with different Valence Band Offset (VBO) namely, nominal case (lower VBO) and higher VBO case. It has been found that high potential barrier heights (ϕ_b) can compromise the performance of the solar cell in terms of FF [OSK11]. This is clearly observed in Fig. 4.14 where the solar cell parameters for two different VBOs are shown as a function of the BSF doping

Table 4.3: Band discontinuities for different heterojunctions formed at the MJSC of Figure 4.1 taken from the literature. All band discontinuities are calculated applying Anderson’s rule. The band discontinuity calculation starts from experimental measurements of the valence band offset or using nominal electron affinities. When electron affinities are used, the resulting band discontinuities are comparable with literature. In the case of the $(\text{Al}_{0.2}\text{Ga}_{0.8})_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ band offset, it is calculated by applying Anderson’s rule [Sil16] but using the nominal electron affinities taken from [Gud+09a; LRS96], respectively. Bold and italic numbers correspond to barriers for majority carriers, electrons (ΔE_{cv}) or holes (ΔE_{vb}). Heterojunctions found in tunnel junctions are not included in this table because non-local tunnelling models (expected dominant transport process) are used to simulate carrier transport instead of thermionic and thermionic-field emission boundary conditions.

Region	Heterojunction	ΔE_{cv} (eV)	ΔE_{vb} (eV)	Reference
Top	GaAs / $\text{Al}_{0.53}\text{In}_{0.47}\text{P}$ (Contact/Window)	0.29	0.65	[Gud+09b]
	$\text{Al}_{0.53}\text{In}_{0.47}\text{P}$ / $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ (Window/Emitter)	0.23	0.32	[Gud+09b]
	$\text{Ga}_{0.51}\text{In}_{0.49}\text{P}/(\text{Al}_{0.2}\text{Ga}_{0.8})_{0.5}\text{In}_{0.5}\text{P}$ (Base/BSF)	0.12	0.15	[ZCF98]
TJ1	$(\text{Al}_{0.2}\text{Ga}_{0.8})_{0.5}\text{In}_{0.5}\text{P}$ / $\text{Al}_{0.5}\text{Ga}_{0.5}\text{As}$ (BSF/Anode TJ)	0.15	0.48	-
Middle	$\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ / GaAs (Window/Emitter)	0.06	0.33	[Gud+09b]
	GaAs / $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ (Base/BSF)	0.13	0.18	[BW86]
TJ2	$\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}/\text{GaAs}$ (Barrier TJ/Buffer)	0.25	0.275	[BW86]
Bottom	GaAs / $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ (Buffer/Nucleation)	0.06	0.37	[Gud+09b]
	$\text{Ga}_{0.51}\text{In}_{0.49}\text{P}$ / Ge (Nucleation/Emitter)	0.01	1.15	[Gud+12]

level. By comparing the lower VBO with the higher one at $N_A=10^{18} \text{ cm}^{-3}$, the difference in FF is about 4% absolute. For higher BSF doping levels, this difference becomes narrower up to a point where FF of higher VBO is very close (1% difference) to the nominal case. It should be mentioned that for a case with nominal band discontinuities (black dashed lines) the FF also improves with doping, but in a lower rate than the high VBO case (about 1% absolute). V_{oc} and J_{sc} remain without significant changes as a function of carrier concentration in any case indicating that majority carrier transport is affected more severely than minority carrier transport through the heterojunction.

Figure 4.14: Solar cell parameters at 5000 suns as a function of doping density of the top cell BSF layer for a high VBO $\sim 700\text{meV}$ (red lines) and for a nominal VBO $\sim 480\text{meV}$ (black dashed lines).

The recovery of FF with the increase of BSF doping level can be explained by looking at Fig. 4.15 where the valence band energy is shown for three cases: a) Nominal VBO, b) Higher VBO and c) Higher VBO with higher doping level than the others. In the nominal VBO case (black dashed lines, nominal band alignment and doping level), the majority carrier transport is better than any other case due to its lower VBO, thus lower ϕ_b (220 meV). As can be seen, a highly doped BSF region (like the green dashed line, $N_A=10^{20} \text{ cm}^{-3}$) shifts the band upwards (Fermi level lies inside the band) and the band bending gets reduced in the BSF, thus its depletion width. This leads to a reduction of the potential barrier thickness enhancing the hole transport by tunnelling through the spike from BSF to the tunnel junction anode, even though ϕ_b is high (480 meV).

Similar dependencies with doping in heterojunctions have been described in [OSK11] on p-type GaAs (base)/GaInP (BSF) heterointerface with a high effective potential barrier (300

Figure 4.15: Valence band energy at equilibrium between AlGaInP/AlGaAs (top cell back-surface field (BSF) and tunnel junction anode). The effective barrier height for each case is: 220 (black dashed line), 430 (red line) and 480 meV (green dashed line). Different transport processes are illustrated such as tunnelling and thermionic emission corresponding to the main mechanisms to overcome the potential barrier formed at the heterointerface.

meV). Although it is not the same heterointerface, the behaviour was similar to Fig. 4.14 showing that higher doping levels were capable to recover the FF on GaAs solar cells. The same procedure was later replicated inside a multijunction structure [KOM10]. Dependencies with doping level for the same heterojunction were also found for a high/low base doping which is different of what we have done here [HB12]. On the other hand, higher doping levels in the lower band gap material may lead to the opposite behaviour as the one shown in Fig. 4.15. The main issue is that at the lower band gap region such as the base layer, the band alignment with the BSF creates an accumulation region (see GaInP base of Fig. 4.15). Then, if doping is increased, the band shifts upwards augmenting the effective barrier height. In this case, neither tunnelling effect nor thermionic transport processes are favoured. In general, a proper optimization of the band offsets and/or carrier concentrations can promote tunnelling or thermionic emission in order to overcome the barriers found at any heterojunction in a multijunction structure.

4.3.6 Voltage loss with light concentration due to perimeter recombination in 3J solar cells

Because the solar cell analysed is very affected by perimeter recombination, especially at the Ga(In)As subcell (see for instance [Esp+15b]) the evolution with concentration of the open circuit voltage losses at the perimeter is shown in Fig. 4.16. In consistency with dark J-V

curves, perimeter recombination reduces the V_{oc} in about 30 mV at one sun, but decreases as a function of light concentration. Indeed, above 1000 suns (where radiative recombination is dominant) the voltage losses due to perimeter recombination are less than 5 mV.

Figure 4.16: Absolute and relative —with respect to 3J— V_{oc} losses due to perimeter recombination as a function of light concentration. The device P/A ratio is 40. Ga(In)As base doping level is $2 \cdot 10^{17} \text{ cm}^{-3}$.

4.3.7 Global optimization

Heretofore, we have not found any significant limitation in a MJSC operating under ultra-high concentration. Some of the limitations discarded with the present approximation include: constraints from top layers where there is high current density, limiting heterojunctions, Auger-limiting processes, high injection effects, etc. In particular, we have shown that a proper tuning of the top layers makes the cell suitable to operate under ultra-high concentration. Accordingly, in this subsection we have carried out an optimization procedure in order to find the most suitable design to work under UHCPV by taking into account all previous results. Furthermore, we have also evaluated the impact of different metal grids in the resulting optimized structure by using typical metal grid parameters found in state of the art multijunction solar cells. The following constraints are considered in the optimization procedure:

1. Top cell emitter doping level has been varied between 10^{18} - $5 \cdot 10^{19} \text{ cm}^{-3}$ and the top cell emitter thickness ranges between 25 to 150 nm, as suggested by Fig. 4.10.
2. Top cell window doping density is fixed at 10^{20} cm^{-3} (see Fig. 4.11) and its thickness is set at 25 nm, which is a value widely used experimentally providing good passivation properties and low absorption in the direct spectrum.

3. Heterojunctions are kept as the ones from the baseline structure for any concentration simulated.

As can be seen in Fig. 4.17, an ideal efficiency peak of 43% is reached at 4,000 suns without considering metal grid losses. If we assume resistive losses corresponding to already achieved front metal contacts, i.e. $R_M=50 \text{ m}\Omega/\text{sq}$ and $\rho_{FC}=10^{-6} \Omega\cdot\text{cm}^{-2}$, efficiencies above 42% can be still achieved for concentrations up to 5,000 suns. In this case, the peak efficiency (42.5%) is reached at 3,000 suns with the following I-V parameters: $J_{sc}=43.7 \text{ A/cm}^2$, $V_{oc}=3.34 \text{ V}$ and $FF=87.5\%$.

Figure 4.17: Efficiency as a function of light concentration of a 1 mm^2 GaInP/Ga(In)As/Ge triple junction solar cell with an inverted-square metallization grid for different metal sheet resistances. The optimized structure has a top cell window doping level of 10^{20} cm^{-3} and 25 nm thickness, the 50 nm-thick top cell emitter doping level is 10^{19} cm^{-3} doped.

As a result of the optimization, it is suggested to use thin (50 nm) and highly doped emitters up to a point where the photocurrent is not compromised ($\sim 10^{19} \text{ cm}^{-3}$). This will be entirely dependent on the prediction of the top cell emitter lifetime as a function of the doping level and dopant used. The lifetime model used for the GaInP may differ to what can be achieved in practice. Nevertheless, we have shown that high efficiency cells for UHCPV can still be obtained ($\eta > 41\%$) by keeping the emitter as usual (see baseline structure) and using very high doping densities at the top cell window layer which would eventually yield a better spreading of the current, and thus efficiency. The highly doped window required is less restrictive in terms of photocurrent due to the low contribution of the window to the final J_{sc} . On the other hand, typical metal grid and front contact resistances are not the main constraint for the cells to work under ultra-high irradiance, as can be seen in Fig. 4.17. Consequently, a proper tuning of the

window and emitter doping and thicknesses is suggested to provide devices operating efficiently under ultra-high irradiances.

4.3.8 Other multijunction solar cell architectures

Previous sections show the potential of the use of ultra-high irradiance in conventional triple junction solar cells based on germanium substrates and using a GaInP subcell as top cell. However, the use of ultra-high irradiance is not limited to just one MJSC architecture. Other high-efficiency cells such as Inverted Metamorphic, wafer bonded cells, dilute nitride cells, etc. can also be considered. In the case of the former, the role of the graded buffer layers must be treated properly to detect if the series resistance of these layers can be an issue. In that case, a proper tuning of the number of layers, doping levels and thicknesses may be required to avoid a significant contribution to the series resistance without compromising the dislocation density and/or relaxation of strain. In the case of the wafer bonded cells, the conductivity of the bonding has already achieved resistances lower than $10 \text{ m}\Omega/\text{sq}$ which is promising [Dim+14]. Higher complexity may be found in next-generation MJSC containing AlGaInP as top cell [Per+15] which has to be tested because going to such a high doping level may lower the collection properties of this material differently than GaInP. Besides, AlGaInP mobilities are lower than GaInP [Ada09]. Anyhow, we have demonstrated that just changing the top cell window doping density is always beneficial when operating under ultra-high irradiance. Regarding the heterojunctions, new systems may appear in any architecture that must be tested theoretically and empirically. Accordingly, any MJSC architecture can be studied by the models and procedures presented here in order to realise multijunction solar cells that operate efficiently ($>42\%$) under ultra-high irradiance.

4.4 Case study 2: Proton irradiation effects on concentrator lattice-matched GaInP/Ga(In)As/Ge triple junction solar cells for space applications

This section presents the experimental results of a 10 MeV proton irradiation on concentrator lattice-matched GaInP/GaAs/Ge triple-junction solar cells and their corresponding component (single junction) subcells. Electro-optical characterization such as external quantum efficiency, light and dark I-V measurements, is performed together with theoretical device modelling in order to guide the analysis of the degradation behavior. The degradation of devices corresponds

to an irradiation fluence equivalent to an 8-years satellite mission in LEO. The information presented here can also be useful for different missions where the irradiance can vary from low to high intensities, i.e., missions to mercury, near-sun missions, among others. This is a result of a group collaboration between IES-UPM and Comisión Nacional de Energía Atómica (CNEA). The author of this thesis contributed mostly to the characterization, analysis and modelling of the devices.

In the past decade, the lattice-matched GaInP/GaAs/Ge triple-junction solar cell (triple junction solar cell (3JSC)) has been chosen for space power generation in spacecrafts and satellites mainly as a result of its high efficiency ($\sim 30\%$ at AM0), relatively high power-to-mass ratio and good radiation hardness [Sta+02; Ada+13; Ima+03]. Other existing multijunction solar cell architectures capable of achieving higher efficiencies than the conventional 3J namely, inverted metamorphic (IMM) solar cells, solar cells including dilute nitride subcells, multijunction devices fabricated through wafer bonding, among others have not yet fully demonstrated neither a radiation hardness comparable to the 3JSC case (see for instance Ref: [Ada+13]¹⁰) nor a feasible and cheap manufacturing process. Despite the good properties of the GaInP/GaAs/Ge 3JSC at beginning of life (BOL), its electrical performance gets degraded when exposed to charged particles in space such as protons and electrons. Obviously, such radiation damage has a deleterious impact on the electrical performance of the cells (mainly via the degradation of their minority carrier properties [Sat+09a]) and hence the analysis of solar cell performance emulating the conditions found in real space missions is a must in order to envisage the optimum configuration of the devices and predict their operation in space.

Although extensive literature exists about radiation damage of 3JSCs [Sta+02; SOI09; Max+13; Sat+09b] the radiation degradation analysis of these cells remains a topic of great scientific interest and debate, as a result of the high complexity of the multijunction structure. Besides, most of the works related to proton damage in multijunction solar cells analyze separately either single junction cells or triple-junction solar cells [Wal+05; Ima+02]. The analysis of each subcell inside a triple-junction has also been studied indirectly by using different irradiation particle energies to control the depth and thus the subcell to be damaged [Ima+02; Sum+03] and by using electroluminescence characterization techniques capable of reconstructing the electrical characteristics of each subcell [Nak+12; Hoh+13]. Even though this indirect technique gives excellent results, it does not provide a direct access to the radiation damage

¹⁰The reader is also referred to recent publications dealing with radiation hardness on IMM solar cells: [Ima+16; Sha+17]

in each subcell. Another motivation to increase the number of degradation studies in conventional 3JSCs is that such structure is the baseline of the so-called 4-junction lattice matched multijunction solar cell which inserts a 1eV cell between the GaAs and Ge subcells [Tho+14; Web].

In this section we expand the experimental data available to understand the degradation in space of GaInP/GaAs/Ge triple junction solar cells and, in particular we do so by analyzing the radiation resistance of devices whose semiconductor structure has been designed to operate under concentrated light. Space applications of this type of devices would also range from near sun missions [Plu08] to alternative space solar panel designs where concentrators are used to reduce the total weight of the panels and increase their efficiency [ONe04]. It should be stressed that devices tested in this work were designed to operate under concentration at about 1000 suns, and this concentration level is probably beyond the actual targets for space concentrator systems. This fact would imply that larger devices should be used for potentially practical applications. Anyway, it is expected that results obtained here will at least hold, given the influence of perimeter recombination in our tiny devices could be considered as not the optimum case for current practical space applications.

In this study, we combine degradation experiments of concentrator triple-junction solar cells (GaInP/GaAs/Ge) together with their corresponding component subcells in the same experiment and report on the effects of 10 MeV proton irradiation at different fluences on these cells. The solar cells have been experimentally characterized in situ –i.e. inside the irradiation chamber– by dark and light I-V measurements and ex-situ by deep level transient spectroscopy, and quantum efficiency. The Technology Computer Aided Design (TCAD) tools described in previous chapters have been used to simulate the solar cells and analyze the experimental findings. The tasks contained in this section were carried out within the framework of a collaboration project with the *Departamento de Energía Solar* (DES) at the Comisión Nacional de Energía Atómica (CNEA) in Buenos Aires, Argentina.

4.4.1 Experimental

10 MeV proton energy is the standard energy used to simulate a space irradiation. The selected fluence represents the fluence received during a space mission in a LEO during 8 years and it was determined using the method previously developed at DES [Alu04].

For this study we grew and manufactured lattice-matched GaInP/GaAs/Ge 3JSCs as well as component cells for each subcell type, namely, single junction GaAs and Ge solar cells together with GaInP/Ge solar cells with active Ge subcells cells (see Table 4.4). The layer design (in

particular, the tunnel junctions and top cell emitter) was adapted to concentrator operation. For further details on the growth see Refs [Gar+09; Bar+09]. Solar cell epiwafers were processed into small area solar cell devices (see Table 4.4) following a procedure very similar to that described in [Bar+09].

All cells received four accumulated fluences reaching a final total fluence of about $5 \cdot 10^{11}$ p/cm². More details are given in [Och+17].

Table 4.4: Solar cell structures subjected to 10MeV proton irradiation. The GaAs solar cells were grown on a highly doped p-type GaAs substrate while the other solar cells were grown on Ge substrates. Two different devices have been irradiated for each solar cell type and their corresponding fluences are shown in the last two columns

Solar cell	Active area (cm ²)	Final fluences	
		(10 ¹¹ p/cm ²)	
GaInP/Ge	0.01	3.35	3.81
GaAs	0.01	2.93	4.99
Ge	0.1	3.59	3.6
GaInP/GaAs/Ge	0.01	3.76	4.78

The cells were characterized ex situ before and after irradiation by quantum efficiency measurements, deep level transient spectroscopy, dark and light I-V (under AM0 spectrum) measurements. More details can be found in [Och+17].

4.4.2 Displacement damage dose analysis

The proton irradiation fluence was converted to the displacement damage dose (D_d^{11}) in order to characterize the radiation response of the solar cells [Sum+94; Mes+01]. Since proton irradiation with energy > 0.1 MeV was performed, it is reasonable to calculate the D_d as the product of the non-ionization energy loss (NIEL) and the particle fluence [Mes+01]. In this case, there is usually a linear dependence between the damage coefficients and the NIEL such as the degradation curve may be explained by a single characteristic curve (i.e. P_{max} vs D_d). Thus, the degradation damage is given by the following semi-empirical expression (see for instance [Mes+01]):

¹¹The D_d is used to correlate the effects of ionizing radiations and provides a means for predicting cell performance from a minimum of ground test data [Sum+94]

$$\frac{P}{P_0} = 1 - C \log \left(1 + \frac{D_d}{D_x} \right) \quad 4.1$$

where D_d is the displacement damage dose in units of MeV/g, P and P_0 can be applied to any photovoltaic parameter (i.e. J_{sc} , V_{oc} , FF and P_{max}) at a dose D_d and before irradiation respectively, and C and D_x are the fitting parameters. To define a criterion of observable degradation, a value of 0.98 for P/P_0 was chosen as a limit taking into account the estimated experimental error. For the calculation of D_d , the GaAs NIEL ($6.588 \cdot 10^{-3}$ MeV·cm²/g for 10 MeV protons [Sum+94]) was used for any material namely, GaInP, GaAs and Ge. This is mainly because of two reasons: 1) for the proton energy used, the NIEL does not vary significantly for the three materials used in this study [WSM00] and 2) for the 3J solar cell; the observed degradation is dominated by the response of the GaAs subcell.

4.4.3 Radiation damage on individual component cells

Fig. 4.18 shows the trend degradation of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and maximum power (P_{max}) observed in situ in Ge and GaAs single junction and GaInP/Ge double junction solar cells at different D_d . In the case of the GaAs cell, it exhibits the highest damage measured. P_{max} starts to decrease for $D_d > 3 \cdot 10^8$ MeV/g showing a power loss of 10% for the final D_d as illustrated in Fig. 4.18(d). The main contribution to P_{max} loss comes from the reduction of V_{oc} (5.7%) while the drop in photocurrent is lower (3%).

Regarding the Ge solar cell, its P_{max} shows signs of slight degradation mainly at final D_d . A V_{oc} loss of about 2% is observed while the photocurrent and FF drop by 1-2% and 1%, respectively. This is equivalent to a P_{max} loss of about 4%. For the GaInP/Ge cell, P_{max} starts to decrease for $D_d > 4.5 \cdot 10^8$ MeV/g exhibiting an absolute loss of about 4% for the final D_d . The overall loss in this cell is a combination of degradation in V_{oc} (0.8%), J_{sc} (0.6%) and FF (1.6%). All solid lines in Fig. 4.18 correspond to the data fitting obtained by using Eq. 4.1 and the resulting fitting parameters are presented in Table 4.5.

Fig. 4.19 shows the dark I-V curves at BOL and EOL for the same cells. The Ge recombination currents at BOL and EOL are almost equal having a slight 10% shift between them which eventually yield to a V_{oc} loss of 3 mV being consistent with Fig. 4.18. Similar results have been found for Ge subcells in a triple-junction solar cell for comparable conditions as the ones used in this study [Sat+09a; Wal+05; Hoh+13; Ohs+06]. The dark I-V curves of 2J GaInP/Ge show larger shifting (30%) to higher recombination currents from BOL to EOL which is equivalent to a 12 mV loss at open circuit conditions also in accordance to Fig. 4.18. This loss can be

Figure 4.18: Degradation in a) J_{sc} , b) V_{oc} , c) FF and d) P_{max} of Ge, GaAs and GaInP/Ge solar cells for in situ measurements at different D_d of 10 MeV proton irradiation. Two different devices are shown for each solar cell type. An experimental uncertainty of 2% can be expected. Solid lines correspond to the data fitting of Eq. 4.1.

Table 4.5: Fitting parameters of Eq. 4.1 to J_{sc} , V_{oc} and P_{max} degradation curves of Fig. 4.18.

	GaInP/Ge		GaAs		Ge	
	C	D_x (MeV/g)	C	D_x (MeV/g)	C	D_x (MeV/g)
J_{sc}	0.5	$4.65 \cdot 10^{10}$	0.64	$2.60 \cdot 10^{10}$	0.03	$1.20 \cdot 10^9$
V_{oc}	0.011	$3.76 \cdot 10^8$	0.06	$4.81 \cdot 10^8$	0.39	$1.73 \cdot 10^{10}$
P_{max}	0.672	$1.63 \cdot 10^{10}$	0.18	$1.27 \cdot 10^9$	0.63	$1.40 \cdot 10^{10}$

attributable mainly to a degradation of minority carrier properties in GaInP and in some extent to the Ge subcell. In agreement with the light I-V curves, the highest damage is confirmed for GaAs solar cells as could be observed in Fig. 4.18 (a), (b) and (d) and Fig. 4.19 where the larger differences between the recombination current at BOL and EOL will be discussed later.

In order to investigate where the damage took place inside the solar cell, EQE measurements have been performed before and after the irradiation. In the case of Ge and GaInP/Ge solar cells, no significant degradation is observed in their photocurrent (lower than 2% and within experimental error), fact that is confirmed with their EQEs (not plotted here). However, the EQE

Figure 4.19: Dark I-V curves for BOL and EOL for GaInP/Ge, GaAs and Ge solar cells.

of the GaAs solar cell shows noticeable differences (which correspond to a 3% current loss) as illustrated in Fig. 4.20(a) along with the corresponding data fitting from TCAD modelling. The degradation of the EQE starts around 600 nm up to the cut-off wavelength. At this region, the dominant photo generation rate (PGR) and the final photocurrent is a mixture of emitter+base contributions as can be seen in Fig. 4.20(b) (the sum of BSF, buffer and substrate photocurrents is too low to be considered). As a result of the PGR calculation, we find that for regions where the emitter is dominant ($400 < \lambda < 550$ nm), there is no degradation of the EQE indicating that most of the damage took place at the base region. Accordingly, in order to fit the EQE at EOL (blue diamonds of Fig. 4.20(a)), only changes at the base region were made and an excellent fit could be attained (blue solid line in Fig. 4.20(a)).

One of the primary consequences of proton irradiation is the physical displacement of atoms that may lead to vacancies, interstitials or even cluster defects all of them creating different energy levels within the gap [Sat+09b; War+10; Tur+13; Mes+13]. These defects can act as traps, recombination centers or as compensation (or carrier removal) sites where the free charge introduced by dopants is localized at the defect effectively reducing the free carrier concentration [35]. Carrier removal is not the radiation damage mechanism in our GaAs solar cells since electrical C-V measurements (not shown here) indicate no significant difference at the base doping level before and after the irradiation ($1.2 \cdot 10^{17} \text{ cm}^{-3}$ and $1.3 \cdot 10^{17} \text{ cm}^{-3}$, respectively). Moreover, carrier removal usually occurs for higher fluences than the ones used here [Max+13; Mes+13]

On the contrary, the formation of vacancies, interstitials or cluster defects is the most probable cause behind the degradation observed [Sat+09b; War+10; Tur+13; Mes+13]. After proton irradiation, the new defects (or native) may change in density and capture cross sections depending on the particle energy and cumulated proton fluence used in the experi-

Figure 4.20: External Quantum Efficiency measurements and corresponding data fitting of the GaAs solar cell before (BOL) and after (EOL) 10 MeV proton irradiation. (b) Calculated photogeneration rate (PGR) of the GaAs solar cell structure. BSF PGR is augmented by a factor of 10^6 . No ARC has been deposited

ments [Ohs+06]. Therein, Deep Level Transient Spectroscopy (DLTS) measurements¹² were performed (not shown here) finding one well defined trap level (hole trap corresponding to a majority carrier trap) located at 0.46 eV from the valence band minima with capture cross section of $4.4 \cdot 10^{-16} \text{ cm}^2$ similar to Refs. [LLK77; ZAI81]. After irradiation, no significant changes were observed in the properties of these defects and no other levels were found. These measurements confirm that deep levels associated with majority carriers do not significantly contribute to degradation after irradiation as expected [Tur+13]. Nevertheless, as suggested by Fig. 4.20(a), the performance losses in GaAs are related to the alteration of the minority carrier trap density and/or properties after the irradiation. To the best of our knowledge, no values of minority carrier defects after proton irradiation experiments in p-type regions have been reported in the literature. There are some studies where DLTS measurements showed the presence of more than one defect level (majority or minority) in n-type regions of p^+n type GaAs cells but nothing related to the study of a p-type region which is our case [War+10; Tur+13; War+04].

¹²DLTS measurements were performed by E. López.

Given the difficulty to measure minority carrier traps, we have overcome the lack of information about the defects properties through numerical simulations. S-R-H recombination is modeled by including a specific defect density located at the middle of the band gap energy [SR52]. In most GaAs solar cells, the recombination losses are dominated by S-R-H recombination at the space charge region and the perimeter both at low forward voltages and at the quasi-neutral regions at high forward voltage bias (above 0.9V for a 1 mm² device) [Och+14]. Even though multiple defects and thus energy levels may arise from 10 MeV proton irradiation, it can be possible that one particular defect level dominates over the others [ZAI81]. In such case, one single defect level would be able to reproduce the EQE as shown in Fig. 4.20(a). In order to fit BOL and EOL data, the bulk defect density of electron traps at the base region has been increased about 30 times from BOL= $5 \cdot 10^{12} \text{ cm}^{-3}$ (resulting in the simulated curve plotted as the black dashed line in Fig. 4.20(a)) to EOL= $1.5 \cdot 10^{14} \text{ cm}^{-3}$ (solid blue line in Fig. 4.20(a)). The higher density of traps reduces the diffusion length of carriers affecting the carrier collection from the base layer and thus its contribution to the EQE.

To provide consistency to the EQE data fitting, dark I-V curves have been computed and fitted simultaneously for the GaAs component cell with the same material parameters and models. A good agreement has been achieved for BOL and EOL for dark I-V curves as can be seen in Fig. 4.21.

Figure 4.21: Dark I-V curves of representative GaAs solar cells at BOL and EOL and their corresponding data fitting. Black lines show the slopes of typical ideality factors of the two diode model.

In order to fit the EOL I-V curve of Fig. 4.21, we have fixed the bulk traps estimated from EQE data fitting and vary the properties of the perimeter. Perimeter trap density has been

increased one order of magnitude, from a surface defect density of $5 \cdot 10^{12} \text{ cm}^{-2}$ to $5 \cdot 10^{13} \text{ cm}^{-2}$. This increase was required to fit the dark current for values below 0.95V while one single bulk defect level was able to fit the curve above this voltage. In such small GaAs solar cells (about 1 mm^2), perimeter recombination dominates the low voltage behavior (no perimeter passivation is employed) and its properties can be modified by proton irradiation.

Despite the possible high impact of perimeter recombination, typical space solar cells have much larger areas (for instance $8 \times 4 \text{ cm}^2$) and hence lower perimeter to area ratios than the solar cell measured here. At higher voltages the fitting is achieved by the increase of minority bulk trap density (as described above) that also degrades the photocurrent as shown in the EQE data [Sat+09a].

In summary, the J_{sc} for single junction GaAs cells is affected mainly by the reduction in the minority carrier properties at the base region due to higher concentration of recombination centers while the V_{oc} reduction at EOL is suggested from modelling to be a combination of losses between: a) recombination centers (70%), and b) perimeter recombination (30%). On the other hand, the loss in V_{oc} attributable to the reduction in J_{sc} is negligible (less than 1 mV) due to the limited fall in J_{sc} (3%). Finally, it is worthwhile to mention that the GaAs solar cell degradation curves of Fig. 4.18 can be corrected for perimeter recombination in order to compare these results with larger space solar cells. If the degradation curves are corrected (neglecting perimeter recombination), they can still be fitted by the same set of fitting parameters shown in Table 4.5. This is mainly due to the fact that perimeter losses do not vary significantly between BOL and EOL (5 mV at V_{oc}) and they lie between experimental error and fitting deviation. This fact provides more confidence when comparing the fitting parameters of Table 4.5 with larger solar cells.

4.4.4 Radiation damage on triple-junction solar cells

In the case of the triple-junction solar cell (Fig. 4.22), the P_{max} starts to decrease at very low $D_d > 7 \cdot 10^7 \text{ MeV/g}$ reaching about 12% loss at the final $D_d (3.15 \cdot 10^9 \text{ MeV/g})$.

Fig. 4.23 shows the EQE of one of the triple junction solar cells before (red lines) and after irradiation (black lines). The GaInP top cell EQE is slightly affected in the base region, which corresponds to a 1.5% loss between BOL and EOL by integrating the product of the $AM0(\lambda)$ spectrum and the $EQE(\lambda)$. On the other hand, the GaAs subcell J_{sc} drops by $\sim 9\%$ in the wavelength range between 700 - 900 nm evidencing a lowering of the minority carrier diffusion length in the base region as the GaAs component subcell case (see black and red dashed lines in Fig. 4.23).

Figure 4.22: Normalized a) J_{sc} , b) V_{oc} , c) FF and d) maximum power output of two lattice-matched triple-junction GaInP/GaAs/Ge solar cells as a function of the D_d . The corresponding data fitting to Eq. 4.1 is shown in solid red lines while the fitting parameters are shown in the inset table.

An interesting effect is observed in the Ge bottom cell, whose EQE seems to increase after proton irradiation. This effect suggests a quenching of the photon coupling between the middle and bottom subcells after irradiation [Bau+07]. Before irradiation, the measured EQE of the Ge bottom cell is artificially low and shows some extra response from 800 nm to 900 nm as a result of photon coupling from the GaAs middle cell [Lim+13]. Once irradiated, the radiative recombination of the middle cell is greatly decreased and an artifact-free EQE of the bottom cell is measured. If the measurement artifact of the EQE before irradiation is corrected [Ste+13c], there is no significant difference between the corrected BOL EQE (blue dashed line) and EOL EQE of the Ge subcell (J_{sc} is 0.4% lower than corrected BOL). The EQE of the Ge subcell at EOL differs in 1.6% from the component cell case, however, it should be kept in mind that the light is filtered by top and middle cells in the 3JSC case and this difference is small enough compared to the measurements uncertainty.

Fig. 4.23 contains an additional evidence to further substantiate the conclusion that the EQE of the triple junction solar cell can be understood just by the superposition of the individual behavior observed in irradiated component subcells. This evidence is obtained by plotting

Figure 4.23: External Quantum Efficiency at BOL and EOL of each subcell of a representative lattice matched triple-junction solar cell GaInP/GaAs/Ge. Dashed blue line shows the EQE of the Ge-subcell after correction. Black and red dashed lines correspond to the EQE measured in the single junction GaAs solar cell. No ARC has been deposited onto the solar cell.

the EQE of fresh (red dashed line) and irradiated (black dashed line) single junction GaAs cells in their overlapping spectral range (600 to 880nm). The EQE of both devices (GaAs single junction and GaAs middle subcell in the triple junction) show an excellent agreement disregarding the oscillations that appear in the GaAs middle cell resulting from the optical interference of the GaInP top cell. This backs the idea that the analysis made for the degradation of the GaAs single junction device also applies for the middle subcell in the 3JSC design.

Fig. 4.24 shows light I-V measurements of a triple junction solar cell device with no ARC before and after the irradiation. As summarized in the inset table, V_{oc} losses are about 70mV after the irradiation which is in agreement with the V_{oc} losses from component subcells GaInP and GaAs (12 mV and 55mV, respectively). Since this is a middle-cell limited device under AM0 spectrum, the photocurrent losses are attributed to the degradation of the EQE GaAs subcell (see Fig. 4.23).

Finally, as can be noticed in Table 4.6, the absolute differences in I-V parameters between BOL and EOL conditions confirm a high correlation between the experimental degradation of triple junction solar cells with their related component subcells.

Figure 4.24: Light I-V curve measured under 1-sun AM0 spectrum of a representative triple junction solar cell at BOL and EOL and their corresponding solar cell parameters. No ARC has been deposited onto the solar cell.

Table 4.6: Absolute differences and relative loss in I-V parameters between BOL and EOL conditions for the solar cells analysed under 1-sun AM0 spectrum. Negative values do not indicate a gain in performance, but values within the measurement uncertainty.

Solar cell	ΔV_{oc} (mV)	ΔJ_{sc} (mA/cm ²)	ΔFF (%)	ΔP_{max} (mW/cm ²)
Ge	3.8	0.86	0.56	0.32
GaAs	54	0.55	-0.07	1.48
GaInP/Ge	11	0.09	0.9	0.42
3J	69	0.39	0.75	1.69

4.5 Summary and conclusions

A 2-D numerical model has been developed and validated for a lattice-matched GaInP/Ga(In)As/Ge 3JSC including tunnel junctions, typical recombination mechanisms (radiative, S-R-H and Auger) and grid metal losses. The validation was carried out at different operating conditions and validated with measurements such as dark I-V curve, light concentration as well as quantum efficiency and reflectance. The subcell I-V curves were also validated through the comparison to EL measurements. A comprehensive analysis of the losses by layers under dark and illuminated conditions was presented as well as the corresponding sensitivity analysis for the validation of the model. Once the model has been validated a couple of case studies were

presented.

In the Case Study 1, the limiting factors of the semiconductor structure design were examined when operating under ultra-high concentration (1,000-5,000 suns). The series resistance components such as those of the top cell window, top cell emitter and heterojunctions have been analysed. It has been found that the window layer may relieve the emitter from high current densities by increasing the doping level (10^{20} cm^{-3}) achieving efficiencies 1% higher than for a lower doping case (10^{18} cm^{-3}). No evidences of high injection effects or Auger-limiting processes have been detected for concentrations up to 5,000 suns with the approximation used here (drift-diffusion models). No important impact from literature band discontinuities have been found for potential barriers formed at heterojunctions from a theoretical point of view. As an example, it has been found that for cases where high band offsets are present; their impact can be mitigated by increasing the doping level favouring the tunnelling of carriers through the potential barriers. The optimization shows the possibility to reach efficiencies above 42% at ultra-high concentration (3,000 - 5,000 suns) by a proper design of the cell. This makes interesting the study of the performance under ultra-high concentration of other MJSC architectures such as Inverted Metamorphic, dilute nitride and wafer bonded multijunction solar cells.

In the Case Study 2, the effects of 10 MeV proton irradiation for an 8-years satellite mission in LEO in concentrator lattice-matched GaInP/GaAs/Ge triple-junction solar cells and their corresponding component subcells have been studied experimentally and theoretically by means of our TCAD modelling. The GaAs solar cell exhibited the highest damage while GaInP/Ge and Ge showed slight signs of degradation at their corresponding final cumulated fluences. The degradation results of the component subcells (individually grown) are consistent with the degradation observed in the triple junction solar cell. The 3JSC losses a 3% in photocurrent while losses in Voc are on the order of 70 mV which corresponds fairly well to the degradation of Ge, GaAs and the GaInP component cells. A single-defect model can reproduce the degradation damage observed on bulk and perimeter of GaAs solar cells for the accumulated fluences used here. However, the presence of multiple defects at different energy levels cannot be neglected. In summary, concentrator solar cell structures show similar results than those of traditional space-targeted designs reported in literature suggesting that no particular changes may be expected if using triple-junction concentrator cells in space.

CHAPTER 5

Four junction solar cell including a dilute
nitride subcell for terrestrial and space
applications

5.1 Introduction

This chapter is dedicated to the study of dilute nitride solar cells and their inclusion into 4J lattice matched structures grown on Ge substrates. First, a brief general introduction of the interesting materials such as dilute nitrides is presented as well as their use in multijunction stacks. Then, a comprehensively experimental and theoretical analysis involving the behavior of dilute nitrides as single junction solar cells is described. Finally, the results of a 4J structure developed by combining MOVPE+MBE technologies are examined including theoretical predictions of its improved performance.

5.2 Background

III-V-N alloys have gathered great interest due to their potential for optoelectronic devices. In such alloys, the group-V element is partially replaced by a small fraction of N that perturbs dramatically the optoelectronic properties of the material. These alloys named dilute nitrides, are classified into the class of semiconductor compounds called highly mismatch alloys (HMAs) with very active research in the past decades. The dilute nitrides are materials that exist in the limit of kinetic stability making the crystal growth a very challenging task even for the most advanced techniques such as Molecular Beam Epitaxy (MBE) or Metalorganic Chemical Vapour Deposition (MOCVD) [Ero08]. The first evidence of N perturbation to crystal lattice was reported back to the 1960's [TH66]. Narrow photoluminescence lines with energy within the forbidden gap were measured for GaP doped with N. Later, N-doping of GaAs was used to modify the emission characteristics of the compound. However, the isolated N energy level in GaAs did not contribute to the luminescence because it lies about 0.25 eV above the conduction band minimum [Wol+85]. Hence, N concentration had to exceed the doping range to modify the emission characteristics of GaAs hindering its application. It was not until the early 1990's when N was successfully incorporated up to a few percent into the GaAs compound by using MOCVD [WSA92; WS93]. This was highly influenced by the development of wide-gap nitrides and the associated technology deployment of N sources and precursors. Indeed, Weyers et al. showed strong red-shift in photoluminescence (PL) energy peaks (up to 170 meV) in the GaAsN alloy by the successfully introduction of minute amounts of N (within the so called

*dilute regime*¹, N=1.4%) [WSA92].

The incorporation of a very different and more electronegative element (N) to a III-V material (i.e. the GaAs compound) leads to a large local perturbation of the crystal lattice potential, affecting drastically the band structure of the material. The most important consequence of N incorporation is the large bandgap reduction with small fractions of N. Even though the bandgap of GaN is more than twice larger than that of GaAs, the bandgap of the GaAsN alloy reduces with nitrogen instead of increasing which would be expected from a linear interpolation between each compound (i.e. GaN+GaAs). In global terms, this is the most unusual characteristic of the III-V-N materials (i.e. GaAsN) which is opposite to what occurs in III-V alloys.

The tremendous and unusual bandgap bowing have been explained by the band anti-crossing (BAC) interaction between the host material and localized states of nitrogen [Sha+99; Sha+04]. The conduction band splits into two nonparabolic subbands (the lower subband, E_C^- and the upper one, E_C^+), being the downward shift of the E_C^- subband the responsible of the reduction of the fundamental bandgap. Additionally to the band structure modification, the changes in the conduction band structure result in significant increase in electron effective mass and large drop in the electron mobility [VR07] which is undesirable for some applications such as photovoltaics. Accordingly, it is now well established that the dependence on alloy composition of the fundamental bandgap of GaAsN is non-linear and does not follow a quadratic dependence as is the case of most III-V alloys which makes the material highly awkward.

The profound reduction of bandgap with N and the possibility to grow alloys that can be formed on GaAs opened up a wide range of applications. For example, after the reported reduction of the bandgap of GaAsN with N incorporation by Weyers et. al, the GaInNAs system was then proposed as a potential candidate for long-wavelength lasers diodes due to its excellent performance at high operation temperature and the possibility to be lattice matched to GaAs [Kon+96].

More recently, besides the GaInNAs system, more complex alloys such as the GaNAsSb and GaInNAsSb have become very attractive materials not only for long-wavelength applications (e.g. photo-detectors, lasers and vertical cavity surface emitting lasers) but also for photovoltaic applications, specially high-efficiency multijunction solar cells. Indeed, next generation lattice matched multijunction solar cells with 4, 5 or 6 junctions demands materials with specific bandgap requirements in the range of 1-1.2 eV [Jon+13]. Accordingly, the most important

¹It is usual to find a classification as follows: ultra-dilute regime (N < 0.01%), the very dilute regime (~0.1%) and the dilute regime up to 10% of N [Hen05; Erk10].

feature of dilute nitride alloys for multijunction applications is the ability to achieve the desired bandgap while preserving the lattice constant to either GaAs, Ge or Si (see Figure 5.1).

Figure 5.1: Band gap energy versus lattice constant for germanium and different III-V (N) alloys. The orange fringe shows the range of desired bandgap for multijunction solar cells with 4 or more junctions on Ge (up to 6) [Jon+13]. Blue lines correspond to the bandgap of dilute nitrides calculated by using the BAC model and parameters taken from [VM03]. Vertical green line is placed at the germanium lattice constant.

5.2.1 Dilute nitrides for solar cell applications

After the successful introduction of nitrogen in GaInNAs by Kondow, it seemed feasible to attempt to grow GaInNAs active layers for solar cell applications. Indeed, dilute nitride 1 eV GaInNAs solar cells were grown by MOCVD at the end of the past century [Fri+98; Gei+98]. Internal quantum efficiencies of about 20% were measured for standard base doping levels (10^{17} cm^{-3}) and up to 60% for lower doped absorbers. Although this carrier collection was not high enough for multijunction solar cells, it allowed to realize of the low minority carrier properties of this material and the strong depletion width dependence of carrier collection. Moreover, (insufficient) improvements in the material quality were observed by changing the growth temperature or by employing post-growth anneals [Gei+98] opening a possible pathway for en-

hancements. Then, attempts to grow the same material by MBE were carried out (see [PFJ02] and references therein). These huge efforts to understand the limitations helped to determine some of the main issues: hydrogen and carbon background impurities, gallium vacancies and deep level defects associated to N [Pta+03]. Despite background impurities and gallium vacancies had some impact on material the degradation, they were not associated to the dominant loss mechanism. Indeed, the unintentional background impurities are about two to three orders of magnitude lower in MBE than MOCVD which favours lower doping concentrations at the absorber. Consequently, historically the highest collection efficiencies have been measured mostly on MBE samples, but may be associated to higher depletion widths rather than a suppression of N-related defects in the MBE-grown material. Although some defect related material properties are found to be different in each growth method (MBE or MOCVD) [Kur+02b], defect structures related to N have not been linked to the growth technique (see [Vol+08] and references therein). Indeed, similar minority carrier properties (lifetimes on the range of 0.4-0.6 ns and Hall hole mobilities about 100-200 cm²/V·s) have been measured for dilute nitride materials, either grown by MOCVD or MBE (see [PFJ02],[Jac+07],[Tho+14],[Gub+14] and section A.2).

At that point, lowering of background impurities that results in larger depletion widths (and possibly higher carrier mobilities) became a pathway to raise the photocurrent generated. Ptak and co-workers at the National Renewable Energy Lab (NREL) were able to achieve very low acceptor concentrations and practically complete carrier collection for MBE-grown 3 µm-thick GaInNAs of 1.15 eV [Pta+05], but no complete carrier collection has been achieved systematically for 1 eV dilute nitrides (a recent publication have demonstrated very high collection efficiency for a 3 µm-thick GaInNAsSb solar cell of 1 eV [MAO17]). Moreover, the achievement of large depletion widths is not easy even by using MBE-growth because some growth parameters need to be well controlled namely, the substrate temperature, the optimization on the use of deflection plates, ions from the radio-frequency plasma source for N, among others [PFK07]. In MOVPE growth, it is even more difficult to achieve large depletion widths due to the unintentional carbon incorporation which is practically unavoidable by using current precursors. Promising research on alternative precursors for MOVPE attempts to mitigate this issue as well as the other key problem of this technology: the low N incorporation efficiency that impedes the use of large precursor overpressure and the related cost increase [Ste+16].

Although high photocurrents have been achieved by reducing the background doping, this is not desirable in high efficiency solar cells because it lowers the V_{oc} (lower quasi-Fermi level splitting for typical minority carrier lifetimes) and it does not remove or annihilate the main loss mechanism such as N related defects. Indeed, bandgap voltage offsets of about 500-700

mV have been frequently reported for dilute nitride solar cells (see [MAO17], [Leo+16] and references therein) indicating that there is still room for improvement (very high quality solar cells are able to achieve $W_{oc} < 400$ mV). Most of the focus is now paid to the annihilation or mitigation of N-related defects as the main loss mechanism. In this regard, thermal annealing treatments have shown a pathway to increase the material quality of dilute nitrides and has become a key step on the development of dilute nitrides for multijunction solar cell applications. Due to this fact, more details on the effect of thermal annealing are given in the following section.

5.2.2 Annealing effects

Despite the interesting properties of dilute nitrides, the successful growth of high quality material suitable for multijunction solar cells (4 or more junctions) is still difficult and has not been completely accomplished. The main drawbacks in the growth of these materials are related to generation of point defects — As antisites AsGa, split interstitials (N-N)As, N-N chain ordering, Ga-vacancies, N-H complex and others (see [Kri+02; Kri+03; Vol+09; Kos+16; Pol+16b])—, high background impurities, phase segregation, inhomogeneities in composition as well as poor structural quality, to name a few (see Table 5.1 for a general summary). While some of those issues can be avoided or minimized by the growth conditions (i.e. V/III ratio, growth temperature, rate or technique) others such as point defects are difficult to annihilate. Besides optimizing the growth conditions, thermal annealing is typically employed to increase the material quality. In fact, it is now well established that *in situ* and/or *ex situ* thermal annealing achieves dramatic improvements in dilute nitrides and it is an imperative process in order to detect significant photovoltaic signatures [MAO17; Lom+17]. This is again, a different behaviour compared to what occurs in other III-V materials [Har+05]. The counterpart is that several complex changes can occur in the structure upon annealing that are not fully understood. Moreover, some of the point defects are not removed by the annealing. Some of the observed general effects are: blue shift of the bandgap (50-100nm), displacement of the junction or type conversion of conductivity (typically p-type material shifted to n-type), increase/decrease of the background concentration, partial removal of N-related defects, among others.

In general, blue shift is extensively reported for different dilute nitrides (i.e. GaIn-NAs[Har+05] and references therein, GaNAsSb [Har+02; Wic+05; Pol+16b] and GaIn-NAsSb[Har+07]). Despite the high level of controversy regarding the mechanisms behind this phenomena, Harris et al. described thoroughly the main candidates from their experiments in QW structures: point defects, NN rearrangement, N diffusion or removal, Ga-In interdiffusion

Table 5.1: Summary of the general requirements and challenges for subcell materials (GaInNAs, GaNAsSb and GaInAsNSb) for 4 or more junctions solar cells on Ge (up to 6)

Requirements	Challenges	Pathways
1 - 1.2 eV	Non-radiative traps	Thermal annealing
Lattice Matched	Charge localization	treatments
High material quality	Growth of coherent layers	Growth technique
Reliable	>1 μ m	Specific growth conditions
Radiation Hardness	Ion damage during growth	Superlattices, QW, DBR's
	Spatial non-uniformities	
	Low background	
	impurities	

and localized depressions in bandgap due to N clusters (see [Har+05] and references therein). Moreover, it is also mentioned that only point defects or NN rearrangement are processes that saturate over annealing time or temperature which results in no further blue shift of the bandgap. However, this does not necessarily implies that if saturation exists, NN rearrangement or point defects are the only mechanisms governing the performance of the material.

Type conversion of conductivity (either non-intentionally p-type to n-type or vice versa) has been reported for several GaInNAs solar cells either grown by MBE or MOCVD [Tuk+16; Kur+04] not only upon annealing but also in different scenarios: with different V/III ratios [Lan+15b], substrate temperature, presence of In or Sb [PFK07], among others. In MOVPE growth, the formation of N-H complex is associated to hydrogen impurities acting as a donor in contrast to the strongly amphoteric nature of H in most other III-V semiconductors [Bro+17]. Although hydrogen has been shown to enhance the surface morphology [OMO02], it has been also related to form complexes with N and H that act as acceptor background impurities [Pta+04].

The annealing may have different effects depending on the material system. In GaInNAs N-As split interstitials and (NAs-AsGa) complex were decreased after annealing (GaInNAs with 30% In content) [KLR15]. In MOCVD, the dissolution of chain-like N-ordering was investigated and correlated to an increase in PL intensity and QE [Vol+08]. GaInNAsSb has shown that Sb may act as a surfactant (under specified growth conditions) that can hinder the formation of defects. Both have shown in different studies the lowering of background carrier concentration (BCC) after annealing. For GaNAsSb, no lowering of BCC was observed after

annealing at 750°C (N ambient) for 15 minutes. The material quality appears to improve and the annihilation of a specific trap level has been identified as the main cause of the improvement (see [Pol+16b]). However, the photocurrent is still far from the desired values in this material. Moreover, a possible increase in the background impurities may occur in GaNAsSb samples that were subjected to a two-step annealing process in our laboratory² (*in situ* + *ex situ* annealing in Rapid Thermal Annealing (RTA) using N₂ as process gas [Lom+17] at different temperatures for 10 minutes). The difference between these two studies is that our samples start to show a hypothetical increase in BCC from 750°C to 850°C. A complete different shape in the QE at the highest temperature suggests that the absorber is indeed higher doped (or similar) than the emitter or even partially converted. No further blue shift was detected in our samples with additional *ex situ* annealing treatments.

All in all, the annealing has shown positive effects such as the lowering of the BCC that increases the depletion width, the removal (or reduction) of vacancies, interstitials and other related defects or complexes. Nevertheless, other nitrogen clusters or defects still remain as limiting factors on the minority carrier diffusion length upon annealing. Therefore, the achievement of very high quality dilute nitrides (comparable to other III-V materials in high efficiency MJSCs) is an extremely complex task.

5.2.3 State of the art multijunction solar cells including dilute nitrides

Presently, lattice-matched triple junction solar cells that incorporate dilute nitrides have reached efficiencies of 44.0% at 942 suns by using a GaInP/GaAs/GaInNAs(Sb) 3J structure grown on inactive GaAs substrates [Jon+13]. For space applications, efficiencies of 31% (AM0) have been already announced [Web]. These efficiencies can be exceeded using a 4-Junction device that incorporates a dilute nitride 1 eV subcell which can be grown on an active germanium substrate. In order to take advantage of the inclusion of a 1 eV dilute nitride solar cell into a 4-Junction structure, the following requirements must be met: 1) J_{sc} of ~ 13 -14 mA/cm² needs to be achieved for current-matching demanding high collection properties in the 1 eV subcell including an efficient broadband anti-reflection coating (ARC) has to be developed and 2) a suitable fill factor. On one hand, to comply with the current-matching criteria, MBE-grown dilute nitrides have shown better photovoltaic properties than their MOVPE counterparts as demonstrated in [Kur+13; Jon+13; MAO17]. However, the quality of the material is very dependent on the optimized growth conditions and specific *in situ* and/or *ex situ* thermal annealing

² The annealing experiments have been performed by I. Lombardero within the framework of his PhD thesis work.

treatments and their effect on the evolution of nitrogen related defects and background impurities [Pol+16a; MAO16a; MAO17; Lom+17]. On the other hand, incorporation of the dilute nitride subcell into the 4-junction stack leads to reduction of the light impinging the germanium subcell. In fact, it compromises the current-matching requirement due to lower carrier absorption/collection of germanium at long wavelengths ($>1600\text{nm}$) and the higher reflectivity at the infra-red region due to the nowadays lack of a broadband ARC. In this sense, recent developments of broadband antireflection coatings have shown superior performance than conventional designs [Per+14; Bue+15], and could be applied to this design of 4J solar cell. All in all, we investigate on the realistic potential of a concentrator 4-Junction solar cell using a $\sim 1\text{-eV}$ dilute nitride subcell grown on germanium active substrates.

In order to undertake the development of a 4-Junction solar cell, we are investigating the combination of both MBE (to grow the dilute nitride) and MOVPE as a first step towards a full MOVPE process. This final approach is desirable because it would reduce the cost per wafer by using monolithically grown cells in a single process with enhanced efficiency.

To date, the quinary alloy (GaInNAsSb) is the most successful absorber material [MAO17] for high-efficiency solar cells while the quaternary GaInNAs has shown also promising results [Pol+16a]. The $\text{GaAs}_{1-x-y}\text{N}_x\text{Sb}_y$ system is the less studied and it is the one we have had access to it through our collaboration within low cost germanium substrates for next generation 4-Junction space solar cells utilising dilute nitride technology (LONGESST) project framework. Therefore, it is the material on which this chapter focus most of the attention as a possible candidate to be used in 4J lattice matched (LM) solar cells.

Accordingly, in this chapter, the advances on modelling and experimental developments towards a 4-Junction including GaNAsSb as a candidate for the $\sim 1\text{eV}$ subcell are described. The chapter is organized as follows: First, we focus on the individual performance of the dilute nitride subcell analyzing theoretically and experimentally the performance of GaNAsSb single junction solar cells. Then, the preliminary requirements for the successful design of the 4J are established. Finally, the first results of the development of a 4J solar cells including dilute nitrides are shown together with projections to explore its short-term realistic potential.

5.3 Modeling and characterization of GaNAsSb single junction solar cells

In this section, the performance of several manufactured MBE-grown GaNAsSb solar cells is analysed theoretically and experimentally. First, we show typical solar cell characterization, then the modelling described in Chapter 2 is used to correlate experimental and simulation results in order to examine the roughly 1 eV-GaNAsSb solar cell. Finally, a set of minimum photovoltaic properties is established and suggestions to improve the performance of dilute nitride solar cells are given.

5.3.1 Device characterization

Four GaNAsSb solar cell structures (see Fig. 5.2) with different absorber thicknesses and doping concentrations have been grown by MBE with nominal compositions of 1.8% and 8.5% of nitrogen and antimony, respectively. Details on the growth can be found elsewhere [Tan+11]³. Three structures have absorber (base) thicknesses of 1, 1.5 and 2 micrometers unintentionally doped (typically p-type with doping level of $5 \cdot 10^{15} \text{ cm}^{-3}$) and the fourth epiwafer has an absorber thickness of 1.5 micrometers with a nominal p-type doping level (Be) of $5 \cdot 10^{17} \text{ cm}^{-3}$. The emitter is an n-type (Si) region with a doping level of 10^{17} cm^{-3} and 100 nm-thick. The p-n junction is surrounded by highly doped GaAs front and back surface field layers as can be seen in Fig. 5.2. The epiwafers were processed into 0.1 cm^2 active area solar cells with no ARC [Och+16d].

The optical and electrical device performance of the GaNAsSb solar cells has been evaluated by means of quantum efficiency, reflectance and current-voltage measurements. The best performance in terms of QE (see Fig. 5.4a) corresponds to a $1 \text{ }\mu\text{m}$ absorber thickness solar cell. This subcell would produce a photocurrent (calculated from the convolution of EQE and the spectral irradiance in the range of 880-1200nm) inside a 4J of 6.25 and 7.75 mA/cm^2 for terrestrial and space spectra, respectively. This is about 60-65% of the photocurrent required in a 4-Junction solar cell for any solar spectrum. The low IQE values in the useful range (880-1200nm) are mainly due to the low diffusion length of carriers measured for these materials as a result of nitrogen-related defects (see [Tan+11] and section A.2.2). As a consequence, solar

³The MBE growth of the samples was carried out by Nanyang Technological University (NTU) in Singapore, Republic of Singapore.

Figure 5.2: Schematic structure of GaNAsSb single junction solar cell. The buffer layer also acts as a BSF layer.

cells with very low doping levels at the absorber are typically used, since their photocurrent is dominated by electric field-assisted collection [Fri+05; Och+16d]. No significant reflectance modifications due to doping or thickness were observed (as the next section will show), as expected.

(a) Experimental IQE of GaNAsSb solar cells with different absorber thickness. Red circles correspond to the only intentionally doped absorber ($5 \cdot 10^{17} \text{ cm}^{-3}$). **(b)** $(hc/\lambda \times \ln(1 - EQE))^2$ curve versus energy. The bandgap is extracted from the x-axis intercept of a linear fit (dashed lines).

Figure 5.3: QE characterization of champion solar cells. Five or more solar cells have been measured showing similar results within typical deviations associated to sample-to-sample variation.

Interestingly, the intentionally-doped absorber solar cell has the worst performance between 880-1200nm while its response improves between 400-700nm. This result is qualitatively in agreement with the fact that the carrier collection is electric field-assisted. A better response at the emitter region is caused by a strong electric field (a minimum value of 40kV/cm has been calculated from our simulations) and a fully depleted emitter due to the lower doping level

(10^{17} cm^{-3}) with respect to the base ($5 \cdot 10^{17} \text{ cm}^{-3}$). The depletion width at the base reduces from 500 to 100 nm being the main cause of the poor response at higher wavelengths (880-1200nm).

Additionally, it has been found that the IQE drops as thickness increases as can be seen in Fig. 5.4a. Our modelling suggests that the IQE degradation with thickness cannot be explained just by electric field-assisted collection and the low diffusion length extracted under the assumptions made here (i.e. uniform doping profiles and uniform material compositions) as it will be detailed in following sections. Thus, a different cause is behind the lower IQE of thicker devices. Possible inhomogeneities in material composition, non-uniform doping profiles or uncontrolled unintentional doping concentrations may be some of the causes and they will be discussed later in more detail.

In the case of illumination current-voltage characteristics, Table 5.2 summarizes the solar cell parameters measured under 1-sun AM1.5d spectrum. As can be seen, the highest fill factor measured is about 65% being lower than expected ($>70\%$) mainly due to the electric-field collection dependence. Open circuit voltages up to 425 mV have also been measured. Considering the effective E_g estimated in Fig. 5.4b by using the Tauc method [TGV66], the bandgap-voltage offset values ($E_g - V_{oc}$) are in the range of 630-660 mV indicating that the material quality has to be improved. For solar cells with very high material quality, 400mV of bandgap-voltage offset is attained [Kin+11].

Table 5.2: Average I-V parameters of the GaNAsSb single junction solar cells. *The epiwafer N2980 has a nominal absorber doping $N_A=5 \cdot 10^{17} \text{ cm}^{-3}$. The standard deviation is shown between parenthesis. Five or more solar cells were measured for each epiwafer.

Epiwafer	W_{abs} (μm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	$E_g - V_{oc}$ (mV)	FF
N2976	2	15.18 (0.79%)	425 (1.42%)	627	64.6% (2.67%)
N2978	1.5	14.3 (1.95%)	392 (4.22%)	655	48.5% (7.46%)
N2980	1.5*	13.4 (1.46%)	367 (1.54%)	660	65.2% (2.74%)
N2982	1	16.04 (1.72%)	412 (1.09%)	630	56.6% (6.48%)

5.3.2 Model validation and analysis

The electrical performance of GaNAsSb MBE-grown solar cells has been also evaluated theoretically. The EQE and reflectance measurements are shown in Fig. 5.4 along with the corresponding simulation data fitting (solid and dotted lines) and the contribution from different semiconductor layers to the total EQE (dashed lines). Two different simulation results by following two criteria are plotted: 1) by modifying two adjustable parameters at the base region such as N_A and $\tau_{e,abs}$ and 2) by fixing N_A to the typical unintentionally doping concentration and adjusting $\tau_{e,abs}$. In the following, we will focus on criteria 1 (data fitting with solid lines) while criteria 2 will be discussed later. As can be seen, at mid-wavelengths (between 700-870 nm), there is a worth to mention disagreement of about 5-6% (N2982), 6-7% (N2978) and 3-4% (N2976) between experimental and simulated EQE. For N2980, a disagreement up to 10% takes place in a wider wavelength region (500-870 nm) and interestingly, the converted shape of the QE due to the modification of the depletion width is qualitatively explained by our calculations —this is an special advantage of the modelling tool used over the semi-analytical approaches—. The excellent agreement between measured and calculated reflectance indicates that the large deviations in mid-wavelengths cannot be attributed to the amount of light reflected by any solar cell (real thickness and measured refractive index have been used, see for instance Appendix A.2). Possible causes of this discrepancy may be related to non-uniformities in the doping profile at the vicinity of the p-n junction or to the role of nitrogen-defects related charge accumulation, which does not follow the classical SRH statistics used. Nevertheless, those deviations are not dramatic and the high quality of the fitting (less than 1% of J_{sc} deviation) in the wavelength range of interest (880-1200 nm) provides a reasonable degree of confidence on the use of the model.

Regarding the QE contributions by regions, most of the carrier collection comes from the space charge region (SCR) (more than 65% in any sample)⁴. In the useful range inside a 4J device, the SCR is more than 80% for all samples disregarding the doped case where the com-

⁴A non-negligible electric field is present at the whole emitter. For the UID samples the lowest value is about 7-10% of the maximum value developed at the p-n junction, however, between the interface with the front surface field (FSF) and the lowest value coordinate there is also a high amount of electric field due to the adjacent wider gap material. We have decided to consider as the emitter the region between the coordinate of the lowest value and the interface with the FSF to distinguish it with the SCR of the p-n junction and the one from the interface with a wider gap material such as the FSF (GaAs). The thickness of the emitter (the so-called quasi-neutral region) is about 60 nm. For the case of the doped material, the emitter is fully depleted by the p-n junction and the lowest electric field reaches values as high as 30% of the maximum electric field at the p-n junction.

plete QE contribution comes from the SCR. There is also a very low contribution to the QE coming from the base (lower than 2% and up to 6% inside a 4J for the best device). It has been detected that some part of the base region is working as an effective recombination zone where there are more recombined electrons than photons absorbed (i.e. negative QE). This means that some of the photogenerated electrons within the depletion region (the p-type zone) are indeed recombined at the quasi-neutral base reducing the total contribution of the SCR.

Figure 5.4: EQE and reflectance for the 4 epiwafers studied in this chapter. The contribution of the different semiconductor layers to the total EQE curve is also depicted (dashed lines). Symbols correspond to experimental curves (circles for EQE and crosses for reflectance). Solid lines correspond to data fitting by modifying the average doping concentration at the absorber (and lifetime) while dotted lines correspond to the fits obtained by modifying only the minority carrier lifetime of the absorber.

We now come back to the IQE degradation with thickness. The fact is that, while the IQE decreases with thickness, the V_{oc} does not follow this trend and changes substantially between samples (see Table 5.2). As mentioned before, fluctuations in element composition as well as uncontrolled depletion widths may be behind the IQE degradation. In the former case, different N and Sb compositions impacts the material quality which is expected to be lower with an increase of the N content. This will decrease the electron diffusion length, thus the IQE. Even though some compositional fluctuations may be present through the structure, it can be deduced that this is not the main reason because the effective E_g (extracted from IQE measurements) seems to be unaffected. Focusing on the devices with unintentionally doped absorber, the differences in the cut-off wavelength are only about 3 meV while the maximum deviation between samples is about 12 meV (i.e. the doped absorber case) as can be seen in Fig. 5.4b. Therefore, although compositional fluctuations are typically found in dilute nitrides, the overall E_g suffers just small deviations suggesting that is not the main cause behind the IQE degradation. Furthermore, any sign of lattice mismatch has been detected either from

Transmission Electron Microscopy (TEM) or X-Ray diffraction (XRD). Additional information has been obtained by TEM measurements showing no structural defects, abrupt interfaces and the absence of significant dislocations at the GaNAsSb/GaAs interface.

Another cause behind the IQE degradation can be related to the inability to grow coherent layers ($> 1\mu m$) in dilute nitrides. This has been ruled out because it would negatively affect the quality of the material, e.g. $\tau_{e,abs}$, which would be unable to explain the measured V_{oc} 's. In other words, the 2 μm -thick device would generate lower photocurrent (which is the case) and lower V_{oc} but as shown in Table 5.2, this device exhibited the highest open circuit voltage. Accordingly, the suggested reason behind this dependence is not related to thickness rather than the effects of unequal properties at the absorber either because of inhomogeneity in the growth or dispersion in the material quality and/or BCC. Because of the complexity to control the depletion widths (i.e. BCC), it is reasonable to expect different BCC after annealing on the samples as well as possible graded doping profiles as already reported for dilute nitride materials [Tuk+16]. Indeed, preliminary electrical C-V measurements reveal a non-uniform doping profile that tends to increase deeper in the base region. Moreover, possible displacement of the physical location of the p-n junction may also occur upon annealing, however, this would also affect negatively the V_{oc} 's which is contradictory to the measured values.

Despite the complexity to control the depletion widths in UID absorbers, it is possible to draw some important conclusions by the correlation of the simulations with the experimental results. Specifically, the correlation between carrier collection and open circuit voltage. Both macroscopic parameters are strongly affected by carrier concentration and minority carrier properties at the absorber providing very useful information of the device performance. The carrier collection provides useful information about the diffusion length of carriers, but also on the depletion width (i.e. unintentional doping). The V_{oc} is useful to deduce minority carrier lifetime, being a good indicator of the material quality and it is also affected by doping concentration. Therefore, we remind that simulations were performed following two criteria: 1) modifying $\tau_{e,abs}$ and fixing N_A to the *nominal* values (fit 1) and 2) varying the two parameters (fit 2).

As can be seen in Fig. 5.4, a very good fitting (specially above 880 nm) can be achieved either by modifying N_A and/or $\tau_{e,abs}$. Both, dashed (criterion 1 or fit 1) and solid (criterion 2 or fit 2) lines are practically equal above 880 nm in all samples. No distinction between the impact of N_A and $\tau_{e,abs}$ can be made just by looking at the IQE. Nevertheless, if N_A is fixed to the typical unintentional value of $5 \cdot 10^{15} \text{ cm}^{-3}$, the predicted V_{oc} 's for the UID devices are lower than the experimental ones as can be seen in Fig. 5.6a (triangles). By increasing the absorber doping concentration, the simulated V_{oc} 's (circles in Fig. 5.6a) are comparable to the

experimental values.

Figure 5.5: Left: Experimental (crosses) and simulated (circles and triangles) V_{oc} for all devices with different N_A and $\tau_{e,abs}$. Right: Difference between quasi-Fermi energies for electrons and holes at the p-n junction for device N2976 at different doping concentrations and electron lifetimes at the absorber. Two different set of parameters of N_A and $\tau_{e,abs}$ that achieved successful QE data fitting are shown. Fixed N_A corresponds to the nominal or UID expected ($5 \cdot 10^{17}$ for N2980 and $5 \cdot 10^{15} \text{ cm}^{-3}$ for the rest.). The electron lifetime fixed corresponds to fit 1 case (70 ps).

V_{oc} increases with doping concentration mainly because of two reasons: 1) the increased $\tau_{e,abs}$ assumed to fit V_{oc} (criterion 2 or fit 2) and 2) the larger quasi-Fermi level splitting (thus higher built-in potential) as shown in Fig. 5.6b. In this case, about 100 of mV are lost because different N_A and $\tau_{e,abs}$. To determine how much of each parameters is involved in the V_{oc} difference we have computed the V_{oc} for sample N2976 by fixing $\tau_{e,abs}$ and varying N_A . Thus, 44 mV are lost by bulk properties while the other 58 mV difference comes from the difference in N_A (close to one order of magnitude, see next section). According to the aforementioned discussion, the modelling suggests that the difference between samples can be attributed to modifications of the BCC for the case of UID samples. Another interesting fact is that the thicker the base region the higher the doping concentration deduced disregarding the V_{oc} (see next section, Table 5.3). This indicates that an increase in the thermal load during the growth of the absorber may lead to higher BCC. For the intentionally doped device (N2980), the better results are also estimated for the case of different doping concentration than the nominal one. In this case, lower doping than the target and extremely low carrier lifetimes have been deduced.

5.3.2.1 Material parameters for model validation

The material parameters deduced are equal in all samples for all regions disregarding those at the base region. In the case of the dilute nitride emitter, the extracted minority carrier diffusion length from the EQE fitting is 82 nm ($\mu_p = 20 \text{ cm}^2/\text{V}\cdot\text{s}$, $\tau_p = 0.14 \text{ ns}$). For N2976 and N2980,

a high interface recombination velocity at FSF/emitter was assumed for both structures ($4 \cdot 10^6$ and $2 \cdot 10^6$ cm/s, respectively). For N2982 and N2978, there was no need to invoke surface states at the FSF/emitter. Regarding the base region, $\mu_n = 33$ cm²/V·s while $\tau_{e,abs}$ was varied as well as the doping concentration as can be seen in Table 5.3. The electron diffusion lengths estimated are: 160, 145, 124 and 48 nm for N2982, N2978, N2976 and N2980.

Table 5.3: Fitting parameters of the absorber region for two different fittings in all epiwafers.

	N2982 (1 μm)		N2978 (1.5 μm)		N2976 (2 μm)		N2980 (doped)	
	N_A	$\tau_{e,abs}$	N_A	$\tau_{e,abs}$	N_A	$\tau_{e,abs}$	N_A	$\tau_{e,abs}$
	[cm ⁻³]	[ns]	[cm ⁻³]	[ns]	[cm ⁻³]	[ns]	[cm ⁻³]	[ns]
Fit 1	$5 \cdot 10^{15}$	0.22	$5 \cdot 10^{15}$	0.1	$5 \cdot 10^{15}$	0.07	$5 \cdot 10^{17}$	0.1
Fit 2	$7.5 \cdot 10^{15}$	0.3	$1.5 \cdot 10^{16}$	0.25	$3 \cdot 10^{16}$	0.18	10^{17}	0.0275

One can ponder about the possible range of values of N_A and $\tau_{e,abs}$ capable of providing the same data fitting. For example, although mobility is also expected to change with doping concentration, a constant value has been used in all simulations mainly because this parameter would affect the carrier collection, but it is not expected to affect the V_{oc} , at least within the range of τ assumed here. Due to this fact, multiple combinations with slight changes in mobility, lifetime and doping concentration can lead to the same results. Interestingly, $\tau_{e,abs}$ for three of the four samples is indeed very similar to the ones already measured in section A.2.2 which suggests that the minority carrier mobilities assumed are reasonable. Another reason of confidence in the parameters of Table 5.3 is that $\tau_{e,abs}$ decreases with deduced doping concentration, as expected. Finally, we would like to draw the attention to the fact that the qualitative results of the data fitting suggests a different BCC at the base region, being systematically higher for the UID samples. Even though BCC can fluctuate or be graded at the base region, in the end the average doping concentration appears to be higher than the typical UID (or lower in the case of the nominal) and it is the suggested reason that explains the measured V_{oc} 's.

In the case of reflectance measurements data fitting, the most important parameters are the thickness of the materials as well as the optical constants. Some modifications in thickness (see Table 5.4) were required to achieve the data fitting of Fig. 5.4. The same optical constants have been used for the UID samples while for N2980 different optical constants were employed to properly fit the bandgap cut-off region. In this case, the optical constants measured for a 10^{17} doped samples (see Appendix A.4) were assigned to the base region. These optical constants exhibit significant absorption coefficient extended to wavelengths up to ~ 1240 nm

(significantly higher *cut-off* than the ones used for the rest of the samples).

Table 5.4: Nominal and modified (in red) thicknesses employed for reflectance data fitting.

	Nominal	N2982	N2978	N2976	N2980
Contact	50	50	50	50	44
Window	40	28	46	35	47
FSF	100	110	110	110	110

In summary, although important limitations on the diagnostic tool (i.e. the non-consideration of non-parabolic bands), uncertainties in some input parameters such as the possible fluctuations of local atomic composition and doping concentration profiles (to name a few), the modelling has shown quite confident results that match reasonably well the experimental data. Indeed, we have shown that the comprehensive analysis of the manufactured set of solar cells through a multiple data fitting of the IQE and V_{oc} suggests that the average BCC is systematically higher than expected for the UID samples. Additional confirmation of these values (average, graded or fluctuations in doping concentrations) are required to: 1) fully validate the modelling tool or 2) show paths for improved modelling by considering another possible mechanisms behind the p-n junction electrostatics.

5.3.3 Analysis of electric field-assisted collection

We will stop briefly to state one of the advantages of physics-based device simulators over analytical approaches regarding electric-field assisted collection. The most important one is that device simulations take into account inherently drift collection (plus diffusion one) that involves directly the effect of electric-field assisted collection without the requirement of any additional calculations. This is an important difference compared to analytical approaches where its inclusion implies unrealistic assumptions or corrections (such as full depletion at the p-junction) [Fri+05]. Indeed, previous treatments of carrier collection in dilute nitrides observed that QE decreases when considering low L_D 's [Fri+05]. In the case of the numerical simulations performed in this chapter, we have observed that QE does not get modified when increasing the thickness (considering also low L_D 's). Despite of the fact that we have observed experimentally a degradation of the carrier collection with thickness, we have shown in previous section that different BCC can be the origin of this degradation. Accordingly, this is an important distinction between approaches that results in very different conclusions that should be taken into

account when examining such devices.

Due to the low carrier collection properties of the solar cells analysed in this section, most of the collected current comes from the space charge region as shown previously, which suggests a high dependence on the electric field. To confirm this dependence, experimental I-V curves in a wider range of reverse voltage bias were performed. As can be seen in Fig. 5.6, the I-V curve show a non-zero slope at small reverse bias—a sort of shunt-like behaviour that does not appear in dark I-V curves—, which confirms the electric-field aided collection and agrees with I-V curves and EQE data in [Fri+05].

Figure 5.6: Experimental light I-V curves using a 940-nm LED – which is only absorbed in the GaNAsSb region – with intensities close to 1 sun (circles) and 2 suns (diamonds). No ARC has been deposited onto the solar cells.

Considering the performance of the GaNAsSb solar cells is strongly dependent on the electric field distribution at the p-n junction, simulations with different base doping levels and thicknesses have been performed to evaluate the impact of the p-n junction configuration. Fig. 5.8a depicts a contour plot of the EQE values at 1000 nm for different base thicknesses (W_b) and doping levels (N_A). Since most of the collection is electric-field assisted, the diffusion lengths of carriers are fixed to the values extracted from Fig. 5.4 (champion design) for all doping concentrations in order to evaluate the impact of different electric field profiles disregarding the diffusion length of carriers. This indeed may be a reasonable assumption according to the similar minority carrier lifetime measured by Time Resolved Photoluminescence (TRPL) (see Appendix A.2.2) for a wide range of doping concentrations (in the range of 0.1-0.5 ns for $N_A=5\cdot 10^{15}$ - 10^{17}). As can be seen, for $W_b > 700$ nm and $N_A > 2\cdot 5\cdot 10^{15}$ cm⁻³, higher doping levels reduce EQE mainly due to the smaller depletion width at the base region (X_p , defined as the depth where the electric field is about 1% of the peak value found at the junction) as can be seen in Fig. 5.8b. For $N_A < 2\cdot 10^{15}$ cm⁻³, that trend is broken and EQE decreases when doping

level is reduced. By lowering N_A from $5 \cdot 10^{15} \text{ cm}^{-3}$ to $5 \cdot 10^{14} \text{ cm}^{-3}$ for $2 \text{ }\mu\text{m}$ base thickness, EQE drops from 49% to 43%. This indicates that carrier collection is not only a function of the depletion width but it is also dependent on the field profile and intensity, as can be seen in Fig. 5.8b where the black line ($N_A = 5 \cdot 10^{14} \text{ cm}^{-3}$) has a larger X_p but shows the lowest electric field peak (18000 V/cm). This also establishes a minimum electric field threshold required to drift carriers across the junction. For N_A similar or higher to N_D (10^{17} cm^{-3}), the collection is very low (32-37%) and almost insensitive to thickness. EQE is also insensitive to thickness for $W_b > 700 \text{ nm}$ and $N_A > 2 \cdot 5 \cdot 10^{15} \text{ cm}^{-3}$ and lower than N_D (10^{17} cm^{-3}) which indicates that for the assumed diffusion lengths, achieved higher thicknesses would not enhance the collection (700 nm absorber thickness is able to get very similar carrier collection than any other higher thickness). Finally, for $W_b < 700 \text{ nm}$ and $N_A < 10^{16} \text{ cm}^{-3}$, the low light absorption reduces substantially the EQE (up to $\sim 10\%$). Although Fig. 5.8a shows the EQE at $1 \text{ }\mu\text{m}$ wavelength, it should be mentioned that very similar contour plots were obtained by plotting the J_{sc} values (not shown).

Figure 5.7: Left: Contour plot of the EQE values at a 1000 nm wavelength as a function of N_A and W_b . Right: Electric field profile across the p-n junction as a function of N_A for solar cells with $W_b = 2 \text{ }\mu\text{m}$. The electric field spans to a depth of $1.2 \text{ }\mu\text{m}$ for clarity.

Accordingly, the current-matching requirement in the current structure could not be met through changes in doping or thickness. Interestingly, the modelling suggests that the reduction in background impurities found experimentally may help to assist carriers but further reduction does not necessarily means higher collection. In practice, lower background carrier concentrations were accomplished ($\sim 10^{14} \text{ cm}^{-3}$) elsewhere and high collection efficiencies were obtained for a GaInNAsSb (see [MAO17]) after an optimization of thermal annealing procedures. This may be contradictory to what Fig. 5.8a predicts. However, although thermal annealing effects usually results in a reduction of the background impurities, it is also reasonable to expect an enhancement of the minority carrier properties. Besides, higher carrier mobilities than the ones

assumed here are expected if doping concentration is reduced. Indeed, Ptak et al. shown very high QEs for GaInNAs even though no post-growth annealing was performed on the samples and mainly because of the very low carrier concentration in the absorber ($\sim 10^{14} \text{ cm}^{-3}$) [Pta+05].

Once the main mechanisms governing the carrier collection are identified, simulations⁵ of QE as a function of the voltage bias were performed in order to derive the required electric field intensity (and profile) resulting in a complete carrier collection for a particular low L_D (see values for N2982 in Table 5.3). As can be seen in Fig. 5.9a, complete carrier collection ($>99\%$) is achieved at -8V for a $1\mu\text{m}$ -thick absorber. At this voltage bias, the electric field applied within the whole absorber is above $E > 2 \cdot 10^4 \text{ V/cm}$ as observed in Fig. 5.9b. This may suggest that having an electric field with magnitude above $2 \cdot 10^4 \text{ V/cm}$ should allow to reach complete carrier collection for any absorber thickness. However, if we look at the carrier collection developed at -8V for a $3\mu\text{m}$ absorber and doped 10^{14} cm^{-3} , incomplete carrier collection of about 85% is achieved although the absorber region is fully depleted with $E \sim 3 \cdot 10^4 \text{ V/cm}$. In fact, notice that a higher doped absorber ($5 \cdot 10^{15} \text{ cm}^{-3}$) is capable of reaching higher carrier collection (empty squares in Fig. 5.9a) than the 10^{14} cm^{-3} one (crosses in Fig. 5.9a) although its absorber is not fully depleted.

Figure 5.8: Left: Carrier collection with zero reflection losses versus thickness of an ideal GaNAsSb absorber (solid line) and calculated values (symbols) of our real solar cells for different bias voltages, i.e. from -8V (blue) to 0.35V (green). Right: Electric field profile across the p-n junction for different bias voltages illuminated with a beam of $1 \mu\text{m}$ wavelength light for two different doping concentrations: $5 \cdot 10^{15}$ (solid) and 10^{14} cm^{-3} (dashed). The thickness of the absorber is $3\mu\text{m}$. Carrier collection is evaluated in the useful wavelength range in a 4J solar cell (885-1200nm) for both ideal and real devices operating at different bias voltages. Each symbol's color of left figure corresponds to the ones of the electric field profile of right figure.

This result is in agreement with previous discussion suggesting that the carrier collection is

⁵Reverse bias breakdown and tunneling transport mechanisms have been neglected.

not only dependent on the depletion width, but also on the gradient of the electric field within the absorber. If the field profile is not favorable, very strong magnitudes of electric field—difficult to get through doping concentrations or gradual doping profiles— are required to achieve high carrier collections. Despite of the fact that very high electric fields exhibit a completely depleted absorber, it is not possible to achieve carrier collections above 85% (see low doped case in Fig. 5.9a). The reason of this fact is the following: considering carrier transport is mainly by drift, the low minority carrier mobility estimated from data fitting —and used in these simulations— is not able to get any advantage of the high electric field. Indeed, by using a carrier mobility about $200 \text{ cm}^2/\text{V}\cdot\text{s}$ (as usually measured in some dilute nitrides by Hall technique⁶, see for example section A.2.1 and [Kur+02a]) the carrier collection at -8V and 0.35V for the low doping case is about 94% and 30%, which is significantly higher than the values shown in Fig. 5.9a. In this sense, the low mobility is in turn the main limitation to achieve high carrier collection. Accordingly, a higher L_D is imperative to take advantage of this dilute nitride structure in very high efficiency multijunction solar cells.

A final note to add is that large depletion widths resulting in high carrier collection do not have the same impact on n-type than on p-type UID absorbers. Indeed, if n-type absorbers (thickest layer) are attained, the depletion width is developed at the back of the absorber where lower photo generation takes place. Therefore, the minority carrier properties requirements are expected to be tougher than those for p-type absorbers where most of the photo generation takes place at the front of the junction in the presence of high electric fields. Moreover, typically the minority carrier lifetime of electrons exceeds that of the holes.

5.3.4 Minority carrier lifetime, mobility and carrier density

The impact of minority carrier lifetime and mobility is now investigated for different doping concentrations. With this, we pursue: 1) to determine the required minority carrier properties to generate the desired photocurrent and 2) to evaluate the impact on solar cell performance

⁶Note that Hall technique measures the majority carrier mobility. It may be reasonable to find such a low minority mobility as the ones estimated from data fitting.

of uniform and gradual doping profiles at the absorber⁷. Although gradual doping profiles are not expected to produce the electric field required to accomplish the J_{sc} target (as shown previously), these simulations are intended to evaluate how much the carrier properties need to be increased to take advantage of a gradual design.

Simulations have been performed on a GaNAsSb solar cell (similar to the structure shown in Fig. 5.2) of 1.04 eV⁸ with a 3- μm -thick absorber (p-type). Five different doping concentrations at the absorber have been considered: 3 of them correspond to uniform doping profiles with values of 10^{17} , $5 \cdot 10^{15}$ and 10^{14} cm^{-3} and the other two, namely LGA and LGB correspond to linear gradual doping profiles. From back surface to top surface, LGA starts from 10^{17} cm^{-3} and decreases linearly to $5 \cdot 10^{15} \text{ cm}^{-3}$ while LGB starts from 10^{16} cm^{-3} and decreases linearly to 10^{14} cm^{-3} . In the case of graded designs, the minority carrier properties were assumed to be doping-independent mainly because of the lack of information. Although this may be unrealistic (specially for carrier mobility), it will allow us to show to what extent gradual doping designs can improve carrier collection by means of its comparison with uniform doping cases. A MgF_2/ZnS ARC optimized to minimize the overall reflection within the absorption range inside a 4J device: $885\text{nm} < \lambda < 1192\text{nm}$ has been assumed. The overall reflection (not weighted by the solar spectrum) is almost negligible with just 0.3% of the incident light that escapes out of the solar cell. This low reflection impacts the photocurrent —calculated with AM1.5d ASTM-G173 solar spectrum— just by 0.04 mA/cm^2 . Therefore, the J_{sc} values shown later can be easily compared to the typical photocurrents developed by any other subcell inside a 4J stack. Moreover, in our calculations the J_{sc} has been normalized to the maximum photocurrent (i.e. ideal IQE) in order to show internal collection efficiencies.

Fig. 5.9 depicts the I-V parameters as a function of $\tau_{e,abs}$ and $\mu_{e,abs}$ for the 5 different cases

⁷For low L_D cases, it may be reasonable to evaluate the impact of bandgap gradual absorbers —or regions with different bandgaps— in such way that carriers can be confined and re-directed to cross the junction. This is of special importance if we take into consideration that the incorporation of Sb in some dilute nitrides could only shift the valence band of the material [Har+07]. Furthermore, the minority carrier properties in dilute nitride absorbers is strongly related to the amount of N in the material. Therefore, a gradual bandgap design with regions of higher bandgap (less amount of N) could possibly attain higher minority carrier properties, thus resulting in improved QEs. Indeed, as previously mentioned, GaInNAs has shown a complete carrier collection for $E_g=1.15\text{eV}$ [Pta+05]. The counterpart is that either the achievement of controlled bandgap regions or gradual doping profiles can be a difficult task because of two main reasons: 1) the complexity to control precisely the desired amount of an element compositions in the material and 2) the bandgap is also influenced by thermal annealing which is a pending issue in dilute nitrides.

⁸Details about the reasons why we chose this bandgap energy value can be found in section 5.4.5

of doping concentrations at the absorber. The main observations are:

- V_{oc} trends are consistent with expected device physics, i.e., higher carrier lifetime and/or hole density (keeping lifetime as a constant) results in higher V_{oc} 's. The maximum V_{oc} is 670 mV and the $E_g - V_{OC} = 370$ mV which is comparable to the state-of-the-art III-V solar cells such as GaInP, GaAs and GaInAs (with E_g of 1 and 0.7 eV) [Fra+15]. The contour lines are mostly flat as a function of $\mu_{e,abs}$ indicating the low impact of this parameter on V_{oc} , as expected.
- The collection efficiency results are also intuitive. Lower restrictions in hole diffusion length are observed for the lowest doped absorbers (i.e. 10^{14} cm⁻³ and LGB) mainly because larger depletion widths. By comparing these two cases, there is no significant lowering restriction if a graded design is used. For example, in order to achieve CE>85%, the lowest $\tau_{e,abs}$ for the highest $\mu_{e,abs}$ is about 0.1 ns for both cases. The most restrictive case is that of the highest doping. For the highest $\mu_{e,abs}$, $\tau_{e,abs}$ should be in the mid-ns range. This case also establishes a minimum mobility required (>40 cm²/V·s) disregarding the $\tau_{e,abs}$ used in these simulations.
- FF shows similar trends with mobility for all cases, being more accused for the lowest N_A . Again, as expected, the highest FF are achieved for the highest doping level.
- The best performance in terms of output power is achieved by a conventional design for mobility values above 100 cm²/V·s. If lower mobilities and high lifetimes (tenths of nanoseconds) are attained, the better performance is observed for the graded designs.

Although the maximum power is achievable with the conventional doping concentration case (10^{17} cm⁻³), low doping designs are typically considered because they are less restrictive in terms of diffusion length. In this sense, this is the most important parameter to consider in dilute nitrides. Once the photocurrent is accomplished, the V_{oc} can be useful and the low FF can be mitigated through enhanced design of the multijunction solar cell (i.e. avoiding its current limitation). Nevertheless, it should be taken into account that a significant amount of V_{oc} would be lost (100-150 mV) because of the reduced built-in potential due to lower doping. Moreover, the route to very high efficiencies is to develop all of their components with the highest possible material quality, so they can approach to S-Q limits or, at least, be comparable to the rest of the III-V solar cells.

Figure 5.9: Set of contour plots representing the I-V parameters at 1-sun AM1.5d ASTM-G173 solar spectrum for GaNAsSb solar cells as a function of both minority carrier mobility and lifetime for different doping concentrations assuming a 3 μm -thick p-type absorber. Both LGA and LGB stand for linear gradual doping (different ranges) from bottom to top of the absorber.

5.4 Modeling and characterization of 4J solar cell

In this section, the performance of a manufactured 4J LM solar cell combining MOVPE+MBE technologies is analysed theoretically and experimentally analysed. Firstly, we show the typical solar cell characterization. Secondly, the modelling previously developed and calibrated for each independent subcell of the 4J GaInP/Ga(In)As/GaNAsSb/Ge in this thesis, is used to examine the performance of the 4J solar cell. Finally, simple but realistic projections based on state-of-the-art devices is carried out as a first approximation to envisage the potential of this 4J structure.

5.4.1 4J solar cell manufacture

The 4J solar cell was developed within the framework of a European project called LONGESST. MBE dilute nitride material (1eV) has already demonstrated higher material quality and has become a promising candidate to be included into a 4J stack.

Two lattice matched GaInP/Ga(In)As/GaNAsSb/Ge solar cells (see Fig. 5.10) have been

developed and grown by combining MOVPE⁹ and MBE¹⁰ growth technologies. One sample (M2367) has a 1 μm -thick GaNAsSb absorber while the second sample (M2366) has a 2 μm GaNAsSb. The motivation to grow different thicknesses of GaNAsSb relies on the unknown impact of MOVPE environment (i.e. the presence of atomic hydrogen and thermal loads) on the material quality. Therefore, the effects of MOVPE growth would be more easily observed in a thicker device (i.e. 2 μm), specially if they benefit the GaNAsSb material quality. Although both the epitaxial growth and the solar cell manufacturing are out of the scope of this thesis, the following aspects are of interest. First, a typical nucleation routine in a MOVPE reactor was carried out on a Ge substrate for subsequent growth of III-V materials. The p-n junction of the Ge subcell is formed by phosphorous diffusion into the p-type substrate during the growth of a GaInP nucleation layer. Then, the tunnel junction was grown and this structure was transferred to the MBE reactor for the growth of the GaNAsSb subcell. Finally, the epiwafer was again placed into the MOVPE reactor for the growth of the second tunnel junction and the two top junctions (GaInP and Ga(In)As). More details on the growth can be found elsewhere [Gar+17b]. Solar cells of 0.1 cm^2 active area were fabricated by conventional photolithography techniques and using gold electroplating for back and front contacts. No ARC was deposited onto the solar cells.

5.4.2 Preliminary device characterization

The performance of the 4J solar cell was evaluated by typical PV-characterization, namely EQE, R, I-V and EL measurements¹¹. Fig. 5.11 shows the EQE measured of the 4J solar cell and control cells used for comparison. As can be observed, the performance of each subcell of the 4J stack (dashed lines) is very similar to the reference control cells (conventional 3J GaInP/Ga(In)As/Ge and 1J GaNAsSb). This is an important result indicating that the integration of the components after the hybrid MOVPE+MBE+MOVPE growth did not affect the EQE of the subcells. Therefore, the multi-reactor approach used to manufacture this structure was suc-

⁹The MOVPE growth of this structure was performed by I. García and the MOVPE epitaxy team at IES-UPM.

¹⁰The MBE growth of this structure was performed by Nanyang Technological University (NTU) in Singapore, Republic of Singapore.

¹¹The PV-characterization was performed at IES-UPM, but in order to evaluate some additional aspects (i.e., calibrated 1-sun measurements, EL.) and for benchmarking, the PV characterization was also performed at NREL (USA) facilities by Mario Ochoa, Iván García and NREL's III-V team. In the case of 1-sun I-V measurements, a calibrated simulator composed by Xe lamp and LED light sources was used.

	Layer No.	Region	Material	Polarity	
J1	1	Win	InAlP	n	
	2	Emitter	InGaP	n	
	3	Base	InGaP	p	
	4	BSF	InGaAlP	p	
TJ1	5	Anode	AlGaAs	p	MOVPE
	6	Cathode	InGaP	n	
J2	7	Window	InGaP	n	
	8	Emitter	GaAs	n	
	9	Base	GaAs	p	
	10	BSF	AlGaAs	p	
	11	Buffer	GaAs	p	
TJ2	12	Barrier-p	AlGaAs	p	
	13	Anode	AlGaAs	p	
	14	Cathode	GaAs	n	
	15	Barrier-n	AlGaAs	n	
J3	16	Contact	GaAs	n	MBE
	17	Window	AlGaAs	n	
	18	FSF	GaAs	n	
	19	Emitter	GaNAsSb	n	
	20	Base	GaNAsSb	p	
	21	Buffer	GaAs	p	
TJ3	22	Barrier-p	AlGaAs	p	MOVPE
	23	Anode	AlGaAs	p	
	24	Cathode	GaAs	n	
	25	Barrier-n	AlGaAs	n	
J4	26	Buffer	GaAs	n	
	27	Buffer	GaAs	n	
	28	Nucleation	InGaP	n	
	29	Emitter	Ge	n	
	30	Substrate	Ge	p	

Figure 5.10: Schematics of the semiconductor layer structure corresponding to the 4J solar cell analysed in this chapter. The MOVPE growth was carried out at IES-UPM facilities while the MBE growth took place at NTU.

cessful in terms of QE performance. In the case of germanium, there is a significant increase of 11% in J_{sc} calculated by the convolution of the EQE with the AM1.5d ASTM-G173 solar spectrum. Nevertheless, this high difference may arise from a different reflectance once the GaNAsSb subcell is introduced into the stack. Thus, it is more difficult to assess some degradation in this subcell, however, it can be stated that the degradation is at least comparable to the one suffered inside the 3J developed at our facilities. Indeed, this has been recently confirmed in [Gar+17b].

Despite the fact that GaNAsSb subcell is 1 μm -thick which results in the incomplete absorption of photons (about 60% according to previous section, see Fig. 5.9a), its low response is mainly related to the low minority carrier diffusion length, as expected from previous results on single junction devices. Besides, as we have shown previously, the EQE of the GaNAsSb would not improve for thicker devices because the low diffusion length forces an effective thickness for carrier collection lower than 1 μm . The low material quality has been also confirmed by spectrally resolved EL measurements. As can be seen in Fig. 5.12, no EL signal has been detected for the GaNAsSb subcell while the rest of the subcells show significant EL intensities,

Figure 5.11: Experimental EQE of a representative 4J solar cell ($1\mu\text{m}$ GaNAsSb absorber) manufactured (solid lines) and the control cells (dashed lines). The control cells are both GaInP/Ga(In)As/Ge 3J cell and a GaNAsSb 1J solar cell. For a proper comparison, the wavelength range used for J_{sc} calculation has been restricted to $\lambda > 885$ nm for the GaNAsSb solar cell and $\lambda > 1200$ nm for the Ge cell and their corresponding EQE's have been cutted for better visualization. For instance, the J_{sc} of the Ge subcell considering the whole range from 885 nm is 10.35 mA/cm^2 .

specially the top junctions. The absence of luminescence at room temperature precludes the use of advanced EL characterization techniques to gain access to internal voltages of the subcells. Anyhow, the modelling we have developed for multijunction structures would help to provide insight into the performance of this 4J solar cell. The rest of the device characterization will be analysed in the following section together with the model validation.

Figure 5.12: Spectral EL for different injection currents showing different light emission and EL peaks coming from GaInP (1.83 eV), Ga(In)As (1.4 eV) and Ge (0.7 eV) subcells. No GaNAsSb light emission has been detected at room temperature.

5.4.3 Model validation and analysis

In order to develop a realistic model for the full 4J including the dilute nitride subcell, we use our previous knowledge of the conventional LM GaInP/Ga(In)As/Ge 3J solar cells with a multi-sun efficiency $\sim 40\%$ (see Chapter 4). Then, we incorporate the GaNAsSb subcell already analysed in Section 5.3.

As can be seen in Fig. 5.13, a quite good agreement has been obtained for EQE, IQE and R by using exactly the same material parameters and optical constants. This demonstrates the robustness and confidence on the model used since about 30 layers with different doping levels, thicknesses, optical constants and related material parameters have been included in the calculation.

Figure 5.13: Measured (symbols) and calculated (lines) IQE (top), EQE (middle) and reflectance (bottom) for the 4J solar cell manufactured by the hybrid MOVPE+MBE technologies.

Nevertheless, there are some important discrepancies to mention. The highest deviation is observed for Ge subcell. Reflectance measurement is very sensitive to slight changes in layer thickness, thus slight non-uniformities would impact severely the measured R, specially for

cases where the light has already passed through a high number of upper layers (i.e., about 25 layers lie above Ge subcell). These fluctuations are also observed for the GaNAsSb subcell and in both subcells it is also reflected in the EQE curve. For the multijunctions analysed here (3J and 4J based on thick Ge substrates), it is important to be aware about those deviations, but keeping in mind that the overall impact is significantly diminished because the Ge subcell is not the limiting one and the GaNAsSb deviation —when calculating its J_{sc} — is only about 2.6% which is reasonable. Moreover, when an ARC is included, those fringes would be smoother and final devices may be modeled more accurately (see further discussion in section 4.2.1.1). Another source of uncertainty derives from the measurement setup as previously mentioned. The influence of spectral resolution, slits apertures, etc., would significantly affect the light reflections. Regarding the simulation of the other subcells —GaInP and Ga(In)As—, the trend is followed more accurately and a good data fitting has been achieved (see Table 5.5).

Table 5.5: Summary of the J_{sc} calculated from the experimental and simulated QE curves for each subcell and by using the AM1.5d ASTM-G173 spectrum.

	J_{sc} (EQE)			J_{sc} (IQE)		
	Experimental	Simulation	Deviation	Experimental	Simulation	Deviation
1 st	10.32	10.42	1.0%	14.29	14.53	1.7%
2 nd	11.18	11.59	3.5%	15.48	14.73	-5.1%
3 rd	5.21	5.35	2.6%	7.25	7.33	1.1%
4 th	10.02	9.18	-9.2%	13.96	12.73	-9.7%

Following our usual methodology, the light and dark I-V curves have to be computed by using exactly the same unified set of models and material parameters. Differently than previous cases (single junction and triple junction solar cells), the 4J structure could not be fitted by using the same set of models and material parameters than the ones used for QE data fitting. Fig. 5.15a shows the experimental light I-V curves under 1-sun¹² AM0 (circles) and AM1.5d (crosses) spectra with the corresponding data fitting (red lines). The black dashed line corresponds to the simulation of the 4J structure (under AM0 spectrum) by using the material parameters extracted from the performance of each single junction solar cell. Then, it corresponds to the expected I-V

¹²It is important to recall that the I-V measurements were taken under a calibrated 1-sun solar simulator at NREL. If uncalibrated simulator is used, high errors in the FF can be expected. Indeed, deviations higher than 15% have been measured. This is mainly because the GaNAsSb was not the limiting subcell under the uncalibrated simulator (see section 5.4.4 for details).

curve of the 4J assuming that the integration of the components was perfect and successful. As can be seen, only J_{sc} has been predicted correctly (about a 10% higher than the calculated from the QE, as observed in detail in next section) while the rest of the curve is significantly different than the experimental case. Even though the QE did not show signs of further degradation than the one suffered in a 3J case, V_{oc} and FF were highly affected. About 400 mV have been lost in the attainment of the 4J and the FF is just 56% while our prediction suggested a higher (but low) FF of about 72.6% (in agreement with values expected from GaNAsSb current limitation). By looking at the dark I-V curve (Fig. 5.15b), a significant shunt is observed at low voltage bias that increases the effective ideality factor up to 10.

Figure 5.14: Left – Experimental (symbols) and simulated (lines) light I-V curves of the 4J solar cell under 1-sun both ASTM G173 and AM0 spectra. An inset table shows the experimental and simulated (inside parenthesis) I-V parameters. Right – Experimental and simulated dark I-V curve of the same solar cell.

The calculated dark and light I-V curves (red lines) are shown mainly to emphasize that one can achieve an excellent agreement to the whole light I-V curve just by fitting the V_{oc} point. Nevertheless, the calculated dark I-V curve has completely different slopes than the experimental one. This indicates that although the L-I-V fitting is quite good, the device performance is not being reproduced correctly. Fitting only one curve separately cannot be considered as a reasonable model validation, specially if one tries to reproduce the behavior of non-ideal devices. Accordingly, the assumptions made¹³ to obtain the L-I-V data fitting can be misleading if one does not look at the dark I-V.

The unexpected origin of the shunt behavior was later analysed by García et al. [Gar+17b]. By comparing single and multijunction devices a decrease of about 140 mV in GaNAsSb V_{oc}

¹³Extremely poor minority carrier lifetimes (on the order of ps for the emitter and tenths of ps for the absorber) and higher mobilities of GaNAsSb (175 and 100 cm²/V·s for emitter and base) were required to achieve QE and L-I-V simultaneous data fitting.

was revealed as well as the fact that Ge subcell also suffered some degradation (about 50 mV which is comparable to the case in a 3J). Moreover, a significant density of micro defects were observed in the epiwafers received after the MBE growth of the GaNAsSb that could explain the remaining 200 mV loss. Indeed, the shunt behavior at low voltages was detected to be dependent on the device size. Lower ideality factors, thus reduced shunt influence was observed in smaller devices (1 mm²) suggesting a decrease of micro defects within the device area.

5.4.3.1 Optical parameters for model validation

An interesting finding has been deduced by fitting the QE of the 4J. The GaNAsSb absorber thickness was reduced down to half-micron (targeted value is 1 μm) in order to fit the Ge subcell curve in the range of the GaNAsSb (885-1200nm). Such a high deviation from the nominal thickness is not expected. Indeed, SEM analysis in previous MBE GaNAsSb samples showed thickness deviations from target values that did not exceed 10%. Another possible reason behind this lower thickness assumption is related to a modification of the absorption coefficient. Indeed, the fitting to EQE and R does not ensure a good estimation of the absorption within the structure which is indirectly deduced by the EQE fitting and well-known optical constants. Nevertheless, it may not be unreasonable to expect that the GaNAsSb refractive index (e.g. absorption coefficient) decreased after the thermal load (and the possible annealing effect) of the two top junctions growth and/or the possible influence of atomic hydrogen. In fact, reflectance measurements performed in our laboratory in a 2J GaNAsSb/Ge solar cell showed very different signatures when subjected to *in situ* annealing treatments (with equal nominal thicknesses) at different temperatures suggesting a modification of the optical properties of the material.

Finally, the thickness reduction of the GaNAsSb was also required to fit the Ge subcell curve (not shown) in the 4J containing a nominal 2 μm -thick GaNAsSb (M2366). In this case, also a 50% of the targeted value was employed to properly fit the response of Ge within the range of the 3rd subcell. Any case, this is still under investigation and more experiments are required to confirm the possible modification of the refractive index.

5.4.4 Shunting behavior of GaNAsSb inside a 4J solar cell

As shown previously, dilute nitride solar cells that have low photocurrents and electric field-assisted carrier collection can be detrimental to the overall performance of a 4J solar cell. This is not only in terms of current matching, but also for the FF . This can be seen in Fig. 5.16a

(left) where the simulated I-V curve of the 4-J device is shown together with the corresponding I-V curves of each subcell. At V_{oc} , all subcells are working in forward bias. At a limiting photocurrent of $\sim 4.7 \text{ A/cm}^2$ and close to the maximum power point (MPP) of the dilute nitride subcell (0.55 V), the shunt-like behaviour of the dilute nitride subcell starts to dominate the 4J device performance resulting in a poor FF (73%).

Figure 5.15: Left – Simulated subcells and complete 4J cell I-V curves under 500-suns AM1.5d ASTM G173 spectrum. Right – Magnification of the region close to short-circuit conditions to highlight the increase in the 4J J_{sc} by summing up the behavior of all the subcell I-V curves.

We have estimated that the FF could recover up to 87% if the 4J solar cell were top cell limited (avoiding current limitation from GaNAsSb and Ge subcell) despite the poor FF of GaNAsSb. However, this would require significant light transfer from the other subcells, reducing the performance of the whole device. Interestingly, the J_{sc} of the 4J does not correspond to the lowest J_{sc} among subcells (that of dilute nitride $\sim 5.7 \text{ A/cm}^2$) but it is indeed higher $\sim 6.3 \text{ A/cm}^2$, about 10% higher. This is because at short-circuit conditions, the dilute nitride subcell is operating under reverse bias (see red points in right graph of Fig. 5.16a) at -2.5V, being this voltage the sum of the other subcells V_{oc} 's. This is attributed to the non-zero slope photocurrent of the dilute nitride subcell both at near short circuit conditions and in reverse bias (between -2.5V and 0V) as a result of the electric-field assisted collection which is dependent on voltage. Similar trends have been already reported for a GaInAsP/InGaAs dual-junction solar cell [Bra+11]. Therefore, it can be concluded that the electric field increases the carrier collection, thus J_{sc} , but it is detrimental for the overall FF of the 4J device. Beyond the obvious but so far elusive way to increase the carrier collection is to improve the carrier diffusion length (i.e., the material quality). Other approaches could be directed towards reducing the length that carriers have to travel to reach the depletion layer of pn junction, for example by using Bragg reflectors to reduce the absorber layer thickness needed.

The band diagram in equilibrium and at critical points (i.e. J_{sc} , P_{max} , V_{oc}) of the light

I-V curve is depicted in Fig.5.16. At J_{sc} , it can be clearly observed how the third p-n junction has a very steep band bending (a high effective built-in potential), being an indicator that it is operating at high-reverse bias accentuated by the low doping density at the absorber. Indeed, at MPP a significant band bending at the GaNAsSb p-n junction is still observed.

Figure 5.16: Energy band diagram at (a) equilibrium, (b) J_{sc} , (c) P_{max} and (d) V_{oc} . Each color corresponds to different regions within the structure of Fig. 5.10. Gray regions contain each tunnel junction with barrier layers (if used) and buffer layers. Note the difference in the vertical axes of these graphs.

5.4.5 Photocurrent requirements

It is typically thought that the 4J over Ge would easily outperform the 3J by simply adding the 1 eV subcell. This is not the true at all mainly because of adding a 1eV subcell implies additional constraints — from the device level point of view — that are going to be described in this section. In general, one of the main disadvantages of the LM 4J solar cell is the constrained flexibility in the bandgaps of the subcells when optimizing for maximum photocurrent. For a proper design, the 4J structure based on GaInP and GaInAs top cells usually requires the thinning of them to maximize the spectrum utilization of the two bottom subcells. Although one can tweak the thickness to distribute the amount of light between subcells, this parameter will always has an upper limit of absorption determined from their E_g . Moreover, and more importantly, E_g is usually the preferred parameter to optimise because it provides higher flexibility on the design for maximization of the photocurrent and substitutes the thinning of the subcells by the use of higher bandgap materials resulting in higher open circuit voltages and fill factors.

The bandgap of a compound semiconductor can be tuned by modifying the composition of their constituents. However, these changes in composition typically involve modifications on the lattice constant of the materials. Considering these premises, the LM GaInP/GaAs/GaNAsSb/Ge stack shows the following characteristics regarding the bandgaps of their components (see also Fig. 5.1):

1. $E_{g,GaInP}$ can be tuned between 1.8-1.88 eV by modifying the ordering parameter either by growth conditions or using Sb without affecting the lattice constant [Str+00; Bar+16]. Besides, a small amount of aluminum can be added to the ternary compound to increase $E_{g,GaInP}$ as long as good minority carrier properties are preserved [Per+16].
2. $E_{g,GaInAs}$ cannot be modified without introducing undesirable lattice mismatch to Ge. As for the case of GaInP, a small amount of Al can also be added in order to increase the bandgap of the material.
3. Dilute nitrides are able to vary its bandgap in a wide range depending on the compound used. Generally, dilute nitrides based on GaAsN (such as GaInNAs, GaInNAsSb or GaNAsSb) offer the possibility to reduce the bandgap from that of GaAs (1.42 eV) to well below 1 eV by increasing the amount of nitrogen (and antimony) in the crystalline structure.

Next generation of these multijunction solar cells (more than 4 junctions) would strictly rely on the addition of aluminum for both top cells (GaInP and GaInAs) in order to modify their bandgap. Aluminum is typically a non-desirable element due to its tendency to oxidize and the formation of DX centers that degrade the material properties. However, to get the desired bandgaps just a small Al amount is required and promising results on these new solar cells have been recently demonstrated [Per+16; Sua+17].

Besides the bandgap considerations that can be tackled through thinning of the subcells, this 4J structure has additional constraints:

- The presence of an indirect material such as Ge will always be less efficient than any other III-V counterpart. Not only because the lower absorption coefficient, but also because the low V_{oc} achieved and the degradation of I-V parameters when subjected to higher thermal loads (see for example [Bar+18; Gar+17b] and section 3.4). Moreover, the Ge subcell does not have any excess of photocurrent as in a 3J case.

- Presently, the best dilute nitride is grown by MBE and the successful development of Ge subcell by MBE has not been demonstrated. Thus, currently the manufacturing of the 4J solar cells implies the use of the hybrid MOVPE+MBE growth.

It should be mentioned that in the particular case of terrestrial applications, the impact of atmospheric absorption bands remains to be studied in detail for this structure. The atmosphere absorption bands lie mainly near the mid-range absorption wavelength of each subcells, specially those found within the 3rd and 4th ones (1400-1500 nm). In the case of Ge, the atmospheric absorption band lies in the plateau region of its QE. Therefore, it is unlikely that any shift due to temperature could affect substantially the subcell J_{sc} . Nevertheless, since the J_{sc} required is difficult to achieve in dilute nitrides, it would set higher restrictions on the design considering atmospheric absorption bands. Consequently, the effect of atmospheric absorption bands is an important parameter that affects the design of multijunctions solar cells, specially those with 5 or more junctions [MFG17].

By considering all the previous constraints and without any modification of the well-known subcells GaInP, Ga(In)As and Ge, we are going to carry out a simple analysis of the 4J J_{sc} to establish the main requirements of the new subcell (i.e. GaNAsSb) in order to maximize the overall J_{sc} . The photocurrents are calculated from their IQE curves, thus no reflection losses are considered. In order to base the calculations on realistic data, measured QE's have been used for Ge, Ga(In)As and GaInP subcells. In the case of the dilute nitride (DN) QE, the following assumption has been made:

$$IQE_{DN}(\lambda) = \begin{cases} 0 & : E_{g,DN} > E_{ph} \\ x & : E_{g,DN} \leq E_{ph} \end{cases}$$

where x is the QE magnitude for all wavelengths which will be varied between 0.5 and 1. For terrestrial and space spectrums, increasing the bandgap of the top cell (or decreasing its thickness) is required to distribute the light in an optimum manner. Hence, $E_{g,GaInP}$ is set to 1.9 eV and Ga(In)As to 1.4 eV and both subcells have been thinned. As a first approximation in terrestrial applications, these top junctions were thinned to produce the 1st target of 14 mA/cm² in order to be comparable to 3J cases where the J_{sc} is typically higher than 14 mA/cm². Then, it was realized that this target is very difficult to achieve because the required dilute nitride QE magnitude is over ~95% (Fig. 5.17a). Therefore, to minimize this complex restriction the target was later reduced to 13.5 mA/cm² (Fig. 5.17b). The target values correspond to the photocurrent produced by the GaInP and Ga(In)As semi-transparent junctions with the corresponding thinning of their absorber regions. Accordingly, the top two junctions were fixed and

simulations were carried out calculating the 4J J_{sc} as a function of two parameters in the dilute nitride: 1) bandgap and 2) QE.

As can be seen by the intersection of the target (red dashed line) in Fig. 5.17b, the real Ge IQE (black dashed line) and the DN QEs, a more reasonable QE target ($\sim 90\%$) is obtained for $E_{g,DN}$ values around 1.04 eV. Therefore, this is the value that will be used hereinafter. Interestingly, the highest J_{sc} is achieved for values higher than 1 eV which is the typical value assumed to increase the efficiency in these structures. It should be mentioned that we have assumed here that temperature dependence of the J_{sc} can be counterbalanced by tweaking the thicknesses of the solar cells thus similar trends may be expected when solving for higher temperatures within the typical range of operation. Nevertheless, if higher temperatures are considered, the best E_g would still be higher than 1.04 eV.

Figure 5.17: J_{sc} of the 4J solar cell by considering measured QE's for GaInP, Ga(In)As and Ge for different dilute nitride QE magnitudes as a function of its bandgap. The cases where Ge is ideal or real (black lines) are also depicted. The calculations have been made at 300K for J_{sc} targets of (a) 14 mA/cm² and (b) 13.5 mA/cm².

Finally, the intention of Fig. 5.17 is not to provide accurate values of the required material bandgap for operation under real specific conditions, but to introduce that there are some other prior constraints that need to be taken into account. Without modifying (e.g. increase material quality or collection efficiency) the other subcells of the stack (specially Ge), very high QEs for the DN subcell are required to take advantage of 4J structure over the 3J case. Tougher restrictions would be present when considering reflection losses.

5.4.6 Germanium subcell limitation and potential enhancements

Because of germanium can become the limiting-current subcell inside multijunction solar cells (e.g, lattice matched with more than 3 junctions or even 3J inverted metamorphic), it is compulsory to evaluate different pathways that could increase its performance. Besides the low V_{oc} ,

the main limitation comes from the very low spectral response of germanium solar cells at long wavelengths. The reason of this is mainly due to the low diffusion length of germanium (see Section A.1.3).

As can be deduced from Fig. 5.18 (solid lines), the conventional IQE of germanium sub-cell (red symbols) is not taking full advantage of long wavelength photons (within the indirect range for $\lambda > 1600\text{nm}$) as the ideal case does (absorption=collection shown by solid lines as a function of slab thickness and calculated by means of: $[1 - \exp(-\alpha L)]$).

Figure 5.18: IQE and absorption calculated using the term $[1 - \exp(-\alpha L)]$, being L the thickness of the germanium slab considered (values in μm) assuming absorption=collection. No FCA was considered and $R_{back} = 0$. Red symbols show a typical state-of-the-art IQE of germanium solar cell with thickness of $150\text{ }\mu\text{m}$ and doped $N_A = 10^{18}\text{cm}^{-3}$.

Increasing the carrier collection could be done by achieving longer diffusion lengths. This could be obtained by lowering the doping concentration of the substrate to increase both, minority carrier lifetime and mobilities. Indeed, if N_A is lowered to 10^{16}cm^{-3} , L_D increases to values $> 300\mu\text{m}$ which would result in a significant increase in the carrier collection. Additionally, the use of back reflectors (BSR) could be considered in order to increase the optical path length (lessening L_D requirement). In any case, it is also possible to consider the use of a BSF layer that could help minority carriers absorbed at long wavelengths (at the back of the solar cell) to travel back to the front junction and increase the collection.

Another interesting subject of research is the use of these kind of structures in space applications. In the case of Ge-based multijunction solar cells, it would be beneficial to reduce the wafer thickness in order to minimize the weight of the solar cell, thus decreasing the launch-

ing cost. Indeed, attempts to reduce the wafer thickness have been already conducted by Ge manufacturers (e.g. UMICORE following guidelines of ESA). In this sense, if the Ge thickness is reduced, it is important to evaluate the absorption/collection of photons as a function of the thickness as well as the surface recombination at the back of the structure.

Accordingly, light I-V curves under 1-sun were computed as a function of the thickness and back surface recombination velocity for two different structures (No ARC has been considered). The first one is a conventional structure while the second one includes a highly doped 300 nm-layer ($N_A = 10^{20} \text{cm}^{-3}$) that acts as a BSF. To illustrate the influence of these parameters, Fig. 5.19 shows the solar cell I-V parameters for both spectra: AM0 and AM1.5d. Following we list the main aspects deduced from Fig. 5.19:

- The general trends in all I-V parameters are similar for both spectra.
- The benefits by the inclusion of a BSF increases with L_D and decreases with thickness, as expected. If thickness is reduced — or L_D is increased — a higher amount of carriers coming from the back of the structure can now be collected, thus benefiting from the BSF influence.
- V_{oc} and FF remain constant with thickness by considering a BSF layer (with significant gains) and disregarding the back surface recombination velocity. This may be attributed to the fact that the BSF acts as a minority carrier barrier reducing the probabilities for electrons to recombine at the back surface.
- For practical purposes, there is a need to obtain low back surface recombination velocities at the BSF in order to maximize the efficiency, given the pursued thickness which is in the range of 20-80 μm .

Although no FCA together with $R_b = 0$ are considered, the results shown previously let us to evaluate electrically the great benefits of including a BSF layer (i.e., up to half percent in absolute efficiency depending on L_D and W_b). Additionally, it is possible to deduce how much can we thin the current solar cells avoiding a significant J_{sc} loss. For instance, the J_{sc} ceases its increase at about 40, 90 and 200 μm for S_b equal to 1000, 100 and 0, respectively for any spectrum. This means that one could thin the device until those thickness values without losing any J_{sc} .

If a back reflector wants to be placed in order to increase the optical path length, the consideration of FCA is a must because it will substantially reduce the reflection capabilities. On the one hand, reducing doping level is one of the pathways to diminish the FCA effects and

Figure 5.19: Ge subcell I-V parameters as a function of base thickness for different solar cell with and without BSF at 1-sun for both spectra: AM0 and AM1.5d. Values in the legends (0,100,1000 in cm/s) correspond to the back surface recombination velocity assumed (S_b). Note the different y-scale for J_{sc} and efficiency for both spectra. No FCA either ARC was considered and $R_b = 0$. The structure without BSF has a diffusion length $\sim 70\mu\text{m}$.

also increases L_D . Indeed, this has been already demonstrated ([Fer+08; Hoh+10]) by using local BSF region (Ge highly p doped with Al) and using low doped substrates (with thicknesses

above 150 μm) to diminish the FCA and increase L_D . An outstanding IQE increase was experimentally demonstrated. Nevertheless, some other concerns arise: 1) low-doped substrates could increase series resistance and 2) high injection effects. Both concerns are more important when operating under high light concentrations. Additionally, lower doping would result in lower quasi-Fermi level (QFL) splitting, thus lowering open circuit voltages. However, the L_D increases substantially with lower dopings (see Appendix A.1.3) because of the increase in both minority carrier mobility and minority carrier lifetime. Therefore, the optimized doping concentration — in terms of V_{oc} — may be a trade off between higher QFL separation and minority carrier lifetimes, as usual in photovoltaic devices. The other possible pathway to diminish the FCA effects is the thinning of the subcell. If the thickness gets reduced, the effects of FCA also reduce and could enable the use of higher doping concentrations.

Extended modelling can be developed by including the influence of a back reflector as well as the effects of FCA. The modelling of a back reflector is straightforward by the simulator, but this will require to deal with incoherent waves in thick germanium as well as FCA. If one intends to optimize such structures in terms of doping concentration, it is compulsory to include FCA effects because the calculation of the photogeneration is considered via the absorption coefficient and its values can be modified depending on the doping concentration. Indeed, a very significant amount of free-carrier absorption is present in germanium layers p-type doped (see [NSM15] and references therein). Thus, in order to calculate the PGR, the FCA (not able to generate electron-hole pairs) should be included for optical calculations (R, T, A) but excluding them for the PGR calculations in a similar as the model developed for silicon solar cells by Clugston et al. ([CB97b]). The inclusion of FCA will be evaluated as possible future feature to be included into the simulator.

5.4.7 Performance projections for space and terrestrial applications

Although GaNAsSb nitride alloy has not fulfilled the J_{sc} requirement to be useful in a 4J solar cell, GaInNAsSb has already demonstrated superior performance [Jon+13; MAO17; Sua+17]. The quinary alloy is rather complex and there is no straight — or fundamental — answer (to our knowledge) to why In leads to superior performance in this alloy over the GaNAsSb one. However, we will attempt to briefly review the literature about the effects of In on the quinary compound and attempt to exhibit the facts already demonstrated in the literature. Then, projections on the performance of the 4J structure including the quinary alloy minority carrier properties (comparable to those of state-of-the-art materials) will be described later.

Although antimony improved GaInNAs material quality and surface morphology, it pro-

vided little improvement to GaNAsSb [Yue+06]. This may be due to the nature of antimony incorporation and the effects of adding indium. Typically, Sb incorporates faster in GaNAsSb than GaInNAsSb. It has been reported that indium favors the reduction of the Sb incorporation, but also introduces strain to the lattice [Yue06]. If indium changes the Sb incorporation, this also may change the material quality. Depending on the Sb composition, the material quality of the alloy may enhance or degrade the performance of the device [Yue+06]. In addition, Yuen et al. also reported that the best material quality in GaInNAsSb has been found by minimizing the incorporation of Sb. It appears that a certain amount of Sb can be negative, being contrary to the typical role of Sb as a surfactant. This is in line with Ptak et al. results showing that a specific amount of Sb affects negatively the GaInNAsSb [PFK07]. Thus, Sb has to be carefully controlled because it competes with In to incorporate into the lattice. In addition, Sb also enhances nitrogen incorporation which can lead to higher nitrogen-related defects. Therefore, the interplay between these atoms (Sb and In) appears to be crucial in the material quality of the quinary alloy. One can assume that many different growth parameters affect the performance of the quaternary and quinary alloys with all of them being strongly related making difficult to draw concise conclusions. Moreover, once a 1 eV alloy is achieved either with GaNAsSb or GaInNAsSb, the thermal annealing treatment is key to further enhance the material quality of these devices and to our knowledge this process has not been fully understood yet.

We now turn back on the potential projections of the 4J including DNs. Fig. 5.20 shows that a ten times increase in L_D (pink line) from the current material L_D (the one of GaNAsSb described in section 5.3) attains a significant enhancement on the DN subcell EQE (85% average). The photocurrent is boosted about 3.8 and 4 mA/cm² for terrestrial and space spectrum, respectively while V_{oc} increases ~ 100 mV and FF goes up to 72% (1-sun values). These solar cell parameters are comparable to the ones already achieved experimentally in other dilute nitrides (GaInNAsSb) by means of thermal annealing treatments [Jon+13; MAO15; MAO16a; MAO17].

Accordingly, in the following simulations we will use a L_D increased by a factor of 10 in the DN subcell in order to estimate the potential and evaluate the performance of the 4J solar cell.

Table 5.6 shows the photocurrent availability for a total light collection (ideal) in each subcell for both terrestrial and space spectra. The photocurrents produced for each subcell calculated from their IQE curves are also shown in order to evaluate their collection efficiency. By looking at the collection efficiency values (percentage values of the available photocurrent between parenthesis in Table 5.6), the GaAs subcell is the one that exhibits the higher perfor-

Figure 5.20: Simulated EQE of each subcell of the GaInP/Ga(In)As/GaNAsSb/Ge 4J solar cell. The EQE's of the GaNAsSb subcell is depicted for four different factors of the current diffusion length (1, 2, 5 and 10). The lower response in the GaAs subcell is due to its thickness thinner (1.25 μm) than usual. A bilayer ARC of MgF2(110nm)/ZnS(70nm) has been assumed and the corresponding reflectivity of the 4J solar cell is shown as a black solid line

mance with about 95% for any spectrum. The GaInP and GaNAsSb subcells achieve similar efficiencies being greater for the terrestrial spectrum than for the space one ($\sim 3\%$). Ge sub-cell shows the lowest collection efficiencies, 75.3% and 81% for terrestrial and space spectra, respectively. Accordingly, there is still room for improvement in any subcell, especially in Ge and to a lower extent in GaInP and GaNAsSb ones.

In order to significantly exceed the efficiency of a 3J by using a 4J solar cell, the additional junction must be close to the state-of-the-art photocurrent values of 3J solar cells. Typically, a J_{sc} of 14 and 17 mA/cm^2 is desirable for terrestrial and space spectra, respectively. As can be seen in Table 5.6, the average value which corresponds to the limiting photocurrent (once the photocurrent is properly distributed) is lower than the desired J_{sc} in any spectrum. In order to improve this photocurrent, the spectral response of the device is examined in Fig. 5.21 where carrier collection, recombination and reflection losses are shown together with the corresponding subcell EQEs and the reflectivity of the 4J solar cell.

There are three important spectral regions for which losses are especially significant where the IQE drops below 85% as illustrated in Fig. 5.21: 1) $\lambda < 500\text{nm}$, 2) $1100\text{nm} < \lambda < 1200\text{nm}$

Table 5.6: Available J_{sc} for each subcell of the 4J structure for space and terrestrial spectra. The calculated J_{sc} from simulated IQE curves (see Fig. 5.21) are also shown for both spectra. A thick absorber ($3\mu\text{m}$) has been assumed exhibiting a 98% of light absorption for all subcells.

Subcell	J_{sc} (AM1.5d) [mA/cm^2]			J_{sc} (AM0) [mA/cm^2]		
	Ideal	From IQE	CE	Ideal	From IQE	CE
GaInP [1.90eV]	16.1	14.0	86.8%	21.9	18.3	83.4%
GaAs [1.41eV]	16.9	16.3	96.4%	18.4	17.6	95.6%
GaNAsSb [1.04eV]	13.6	11.7	86.0%	17.7	14.7	83.3%
Ge [0.67eV]	15.5	11.6	75.3%	20.9	16.9	81.0%
Máx.	15.5	13.4	86%	19.7	16.9	86%

Figure 5.21: Simulated external quantum efficiency (black dashed lines) of the 4J subcells. The corresponding reflectance is shown by a solid gray line. The region where photons are lost by recombination is shown in blue while the region corresponding to reflection loss is shown in red. Each junction has enough thickness to absorb above 98% average of the incoming light in their corresponding wavelength range. In the legend, a summary of collected and lost photocurrent is depicted.

and 3) $1500 < \lambda < 1800\text{nm}$. In region 1, the high J_{sc} loss ($\sim 15\%$) is mainly due to surface recombination and window/emitter interface recombination, as expected. In region 2, the loss is mainly related to the diffusion length of carriers in GaNAsSb while region 3 is related to the indirect bandgap of Ge and its low absorption coefficient as well as the low diffusion length

of carriers. In the case of Ge, the use of advanced Ge solar cells by employing low-doped Ge substrates that improves the carrier diffusion length as well as diminishes the free-carrier absorption at long wavelengths has been already reported [Fer+08; Hoh+10]. This, together with the use of a possible local BSF and a back reflector could be one of the pathways to improve the long wavelengths response in Ge. For concentrator applications, the series resistance — and possible— high injection effects have to be evaluated due to the low-doped Ge substrate.

Table 5.6 and Fig. 5.21 give an idea of the impact from atmospheric absorption bands in the infra-red region while considering AM0 and AM15d spectra. For example, for Ge the collection efficiency is 6 points higher under AM0 over AM1.5d. This is mainly because the water absorption in terrestrial spectrum lies on the region where the QE is high and lower recombination losses are depicted. Conversely, the observed dip in the spectrum near 1100-1200 nm affects less severely the dilute nitride since it lies in a region where the recombination losses are higher, thus poorer collection is expected. Anyhow, the effect of atmospheric absorption bands is an important parameter that affects more severely the design of multijunctions with 5 or more junctions [MFG17].

Assuming no further improvements in the present 4J device, it is important to mention that there is a pathway to mitigate the recombination losses in terms of photocurrent. This is of special importance in the case of 3rd and 4th junctions as shown previously. For example, the amount of electrons generated and lost by recombination at a specific wavelength region (close to the bandgap edges) can be mitigated by using a different with higher collection efficiency. For example, in region 2 ($1100\text{nm} < \lambda < 1200\text{nm}$), the GaNAsSb subcell has high recombination losses as can be deduced from the large blue region and the decreasing EQE. However, germanium is capable of taking advantage because it is more efficient than GaNAsSb in this wavelength range which has been deduced from the 90% average IQE of Ge (not shown). The same reasoning applies to favor the GaNAsSb, but in the GaAs region close to its bandgap. In this region, the IQE of GaNAsSb is higher than at any other higher wavelength. Obviously, this would involve the thinning of the corresponding junctions.

Light I-V curves have also been computed as a function of subcell thicknesses in order to optimize the performance of the solar cell. As can be seen in Fig. 5.23, for a 4J solar cell representative of Fig. 5.22 whose ARC does not provide low reflectivity in the whole spectrum range the peak efficiency is $\sim 44\%$ within the 1000-2000 suns range (red dashed line). In this respect, further increase can be achieved by taking advantage of the low reflectivity offered by a broadband ARC ($< 5\%$ in the whole spectrum range) as already demonstrated in [Per+14; Bue+15]. By including this improved ARC and tweaking absorber thicknesses to redistribute

Figure 5.22: Simulated External Quantum Efficiency and reflectivity of the GaInP/GaAs/ Ga(In)NAs(Sb)/Ge 4-J solar cell analysed in this thesis. The structure assumes a conventional $\text{MgF}_2(110\text{nm})/\text{ZnS}(60\text{nm})$ ARC (gray line). The improved ARC taken from [Per+14] is represented by a black dashed line

the subsequent gains in photocurrent, the projected peak efficiency would be $\sim 47\%$ at 1000 suns (green line), with the improvement mostly resulting from the increment in J_{sc} (12.8/13.7 mA/cm^2) and to a lower extent in V_{oc} (~ 8 mV at 1000 suns). Above 2000 suns, series resistance due to the front metal grid starts to limit the performance. The results of Fig. 5.23 correspond to the present material quality of these devices intending to provide realistic efficiencies that can be achieved in the short-term.

Regarding space applications, we have set the top cell as the responsible of the limiting photocurrent which is also a good rule for EOL since GaAs solar cells are the most affected by the radiation environment while GaNAsSb subcell has not been tested yet. Having a slightly current mismatch increases the overall FF [McM+08], specially if a large bandgap junction is the one limiting the photocurrent. The estimated efficiency for this structure is 31.4% with a $J_{sc}=16.5$ mA/cm^2 , $V_{oc}=3.2\text{V}$ and $FF=83\%$. By using the improved ARC and refining the structure design, there is potential to boost the efficiency above 33%. Despite the numbers given here, it is important to note that the final values are very dependent on the spectral response of each subcell and the ARC design. There is some degree of flexibility if one can vary the top cell and dilute nitride bandgaps as well as the thickness of each junction. Finally, the ARC must be designed taking into account the spectral response of each subcell.

Figure 5.23: Performance as a function of concentration of the optimised 4J solar cell under AM1.5d ASTM-G173.

5.5 Summary and conclusions

The potential of lattice-matched 4J solar cells including dilute nitride subcells for both terrestrial and space applications has been studied. First, a full validation and analysis of dilute nitride single junction solar cells with different absorber thickness and doping concentrations was carried out. The GaNAsSb solar cells analysed here exhibited low diffusion lengths and the electric field plays a key role in the carrier collection. It has been found experimentally that the QE of the device reduced significantly with thickness. Possible inhomogeneities in material composition, non-uniform doping profiles or uncontrolled unintentional doping concentrations may be some of the causes. In fact, a correlation between QE and V_{oc} data fitting from a flat-doping model to several solar cells suggested a slightly higher than nominal doping concentration — in average — in order to explain the V_{oc} and reduced QE with thickness. This is mainly because a lower doping concentration reduces the depletion width of the pn junction, thus the carrier collection. Then the model was used to assess that with the present minority carrier properties it is not possible to achieve the photocurrent requirements for this solar cell to be included into a 4J device. Additionally, the photocurrent requirements inside a 4J solar cell were carried out for both the dilute nitride showing that very high QEs ($<90\%$) are required if state-of-the-art spectral responses are used. Indeed, the germanium subcell can be the limiting one. Therefore, a simulation campaign was carried out in order to show possible pathways to optimize the spectral response of germanium solar cell.

Secondly, a realistic modelling of the GaInP/Ga(In)As/GaNAsSb/Ge 4J solar cell has been developed departing from an extensive dilute nitride material characterization of the GaNAsSb material we have used. The modelling shows that the shunt-like behavior, caused by the electric field-assisted carrier collection, and the low FF of the GaNAsSb subcell substantially degrade the performance of the 4J solar cell. This limits the potential of using the electric field-assisted carrier collection and indicates that the clearer (but so far elusive) path to achieve very high efficiencies is to improve the diffusion lengths of minority carriers by improving the quality of the dilute nitride subcell. By using the minority carrier properties of the best dilute nitride solar cells found in the literature (GaInNAsSb), the optimization results in efficiencies above 47% at 1000 suns and 33% for concentration and space applications, respectively. In order to realize these efficiencies, a broadband antireflection coating is required. Finally, preliminary lattice-matched 4J GaInP/Ga(In)As/GaNAsSb/Ge solar cells have been fabricated by using the hybrid MOVPE+MBE growth. It has been shown that the integration of subcell components using this multi-reactor approach produces no degradation of the IQE of the subcells, but strong V_{oc} loss was measured. This is encouraging towards the attainment of a fully MOCVD process for the growth of the 4J structure.

CHAPTER 6

Influence of temperature on luminescent coupling in multijunction solar cells

6.1 Introduction

This chapter deals with the influence of temperature on the luminescent coupling in inverted lattice matched and metamorphic multijunction solar cells. First, an introduction to the luminescent coupling and a brief review of the literature are presented. Following, luminescent coupling analysis is shown as a function of temperature in two tandem components of an inverted metamorphic triple junction solar cell such as GaInP/GaAs and GaAs/GaInAs solar cells. The results are quantified and examined by means of luminescent coupling analysis and modelling, electroluminescence measurements and optical modelling at the device and subcell level. The results of the models are experimentally verified and discussed.

6.2 Background

State of the art III-V solar cells contain very high quality materials being radiative recombination the dominant loss mechanism. This implies that the light received by the solar cell is re-emitted in a significant amount — with energy close to the material bandgap — and can be re-absorbed internally producing new electron-hole pairs. In general, photons are emitted at all angles and they can be re-absorbed in the same layer of emission or by any other layer of the semiconductor structure with a lower bandgap. If the re-absorption takes place at the same layer of emission, the process is known as photon recycling (photon recycling (PR)) or self-absorption. If the re-absorption occurs in a different layer where the emission takes place, the process is known as optical coupling [LHB06] or also called luminescent coupling (hereinafter LC). Both phenomena (PR & LC) are illustrated in Fig. 6.1.

The principles governing PR and LC are the same and the first studies date from the mid and late 1950's for germanium and InSb materials [Hay55; Dum57]. A thorough historical review of photon recycling phenomena can be found in [Bal04]. Although the concept was introduced in the 1950's, it is a phenomenon difficult to measure and quantify. Furthermore, PR becomes significant when radiative recombination is dominant or at least comparable to non-radiative recombination. It was not until the eighties of the last century when III-V solar cells started to demonstrate very high material quality to take advantage of PR facilitating its detection. More recently, at the beginning of this decade, it has been demonstrated that PR is the key factor for the development of record solar cells operating close to the fundamental limits [Kay+11; Ste+13a]. In the case of LC, it was not until the development of high-quality multijunction solar cells that started to be experimentally confirmed and examined profoundly.

Figure 6.1: Schematic for a dual junction solar cell showing the photon emission from radiative recombination and the re-absorption of such photons in the same subcell (PR) or the lower bandgap subcell (LC).

Therefore, LC has become an important object of very active research in the past decade (see for example: [Bau+07; SG12; Ste+13b; Ste+13c; FGS13; Lim+13; Sog+13; Li+13; FGS14; Shv+13; Wil+14; Ren+15; Lan+15a; Wil+15; Ste+15; Shv+16; Jia+16; Yua+16; Och+16b; KFS17]).

The implications of PR and LC in single and multijunction solar cells are different. Photons re-absorbed in the same junction effectively reduce the radiative lifetime increasing the open circuit voltage of the devices [Asb77; MBR97]. Photons emitted by one junction and absorbed by another can contribute to the photocurrent of that junction [SG12]. In single junction cases such as GaAs, the generation of photons by layers, i.e. the substrate, and the re-absorption of those photons by active layers can have an impact on the spectral response close to the bandgap cut-off [LHB06]. Although its impact is very small, it helped to confirm the concept. For multijunction solar cell cases, as the ones studied in this chapter, the spontaneous emission from upper junctions can contribute significantly to the photocurrent generated by junctions underneath altering the device design.

Therefore, the effects of LC are important in the design and characterization of multijunction solar cells. In some cases, typical tails found in spectral response measurements are now attributed to LC [Bau+07; Lim+13]. There are also important implications on measuring the I-V curves because QE is typically used to set the simulator spectrum [Ste+13c]. Other advanced characterization techniques such as electroluminescence (widely used presently to get internal voltages of each subcell) are affected as well [Kir+08; Gei+14]. In general, in the presence of LC, additional considerations must be attained for any characterization technique of

multijunction solar cells.

As mentioned before, the impact of LC is not only important in terms of characterization, but also on the design of multijunction structure for optimum performance. Friedman et. al showed that subcell optical thinning in a two-junction device may not be required for current-matching. Their calculations were performed at ambient temperature and estimated an increase in efficiency less than 1% depending on the LC strength [FGS13]. Another consequence is that the additional photocurrent modifies the optimal bandgaps altering the current matching and having strong implications in the fill factor minima as a function of the light intensity [FGS14]. Therefore, more accurate designs of high-quality multijunction solar cells require the full consideration of LC and its variation under real operating conditions. Because of the importance of studying devices under real operating conditions and since LC has been studied thoroughly by other authors under laboratory and specified conditions¹, we study empirically and theoretically how the LC is affected by varying one of the most important parameters to consider when working under real conditions: the solar cell temperature.

6.2.1 Influence of temperature on MJSC performance

The operating temperature in a solar cell has a strong impact on its performance and reliability [Esp+15a]. In a photovoltaic system, the cell temperature is affected by many factors such as: ambient temperature, irradiance, wind speed and the heat extraction properties of the module [SB14; Alg07]. The accurate measurement of the cell temperature is a difficult task but, in most cases, the estimated operating temperature of multijunction solar cells working under concentrated illumination is in the range of 50-80°C [Rod+14]. In some cases, especially for large cells, the cell can reach temperatures above 100°C [Kin+08]. Therefore, the design of concentrator solar cells must consider its real operating temperature in order to maximize the electrical output in the field.

Different physical phenomena occur when the cell temperature increases, namely: 1) reduction of the bandgaps of the semiconductors in each subcell which determines how much light is absorbed in a subcell and how much light is transmitted to the underlying subcells thus changing the photocurrent of the multijunction cell; 2) decrease of the open-circuit voltage as a result of the reduction in bandgap; 3) variation of the refractive index and absorption coefficient; 4) change in the majority free carrier concentration affecting the electrical and thermal

¹See also [Gei+15a] for calculations of the energy yield of concentrator solar cells by varying spectral conditions and temperature and considering the impact of LC.

conductivity; 5) depletion of deep level defects that increases the non-radiative recombination current; 6) decrease in the minority carrier diffusion length, mobilities, etc. In the end, all these variations result in a worse solar cell behavior at high temperatures [GVA16b].

Recently, Inverted Metamorphic (IMM) multijunction solar cells have reached efficiencies close to 46% [Pre] and are candidates to achieve 50%. The influence of temperature on these cells was studied by Steiner et al. [Ste+11] who showed the efficiency of a triple-junction (3J) IMM solar cell at moderate concentrations drops by around 6% absolute when the cell temperature increases from 25°C to 126°C. The consideration of LC affects the structural optimization of the solar cell in terms of critical aspects such as thicknesses and bandgaps of the subcells [FGS13; FGS14]. Therefore, the effect of temperature on LC is required to be known for any multijunction solar cell design. Indeed, higher annual conversion efficiencies and higher immunity to spectral variations have been modeled by considering some of the temperature effects on LC presented in this chapter [Gei+15a]. To fill this knowledge gap², the dependence of LC with temperature is analysed in this chapter within a typical range for real operating conditions (25-120°C).

The chapter is divided as follows: Section 6.3 describes the experimental procedures involved on the LC characterization as well as the samples to be studied. In section 6.4, the LC characterization results are analysed. Then, the description and results of the LC model by considering the influence of temperature are explained in section 6.5. Finally, an evaluation of the material quality through optical modelling and subcell characterization as a function of temperature is presented in section 6.6.

6.3 Experimental

All characterization was performed in the framework of a research stay of Mario Ochoa (spring of 2014) at the National Renewable Energy Laboratory (National Renewable Energy Laboratory (Golden, CO, USA) (NREL)) in Golden, CO, USA. Characterization of all samples was performed at NREL facilities.

²Additional studies on characterization of LC as a function of temperature have been reported from the development of our work in 2014 which was electronically published in 2015 [Och+16c] and the time of writing this document. We must refer the reader to the work developed by Shvarts et al. in 2015 [Shv+15].

6.3.1 Sample description

Two inverted, dual junction structures, namely ML732 and MM708, were grown in an atmospheric pressure MOVPE reactor [Gei+07]. ML732 is a $\text{Ga}_{0.51}\text{In}_{0.49}\text{P}/\text{GaAs}$ tandem grown lattice-matched on GaAs and MM708 is a $\text{GaAs}/\text{Ga}_{0.75}\text{In}_{0.25}\text{As}$ metamorphic tandem grown on GaAs as shown in Fig. 6.2

Figure 6.2: Design of the two structures analysed. The solar cell active areas are 0.25 and 0.1 cm² for ML732 and MM708, respectively. Horizontal axis indicated the lattice constant.

The solar cells were manufactured using conventional photolithography and metal deposition techniques whose details can be found in [Gei+07]. A MgF_2/ZnS dual layer ARC was deposited onto the ML732 device by thermal evaporation while no ARC was deposited onto the MM708 device. The GaInP top cell in the ML732 device has the rear heterojunction (RHJ) design described in [Gei+13], which has been demonstrated to lower the space charge region recombination. The other two subcells (GaAs and metamorphic GaInAs) follow traditional designs [Gei+07]. In order to enhance photon recycling and luminescent coupling inside these solar cells, the substrate was removed in both structures and a highly reflective gold mirror was electroplated at the back side of each cell. A highly doped $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ layer for the ML732 and a 1 eV GaInAs layer for the MM708 were grown to achieve a p-type ohmic contact with gold.

In order to carry out the LC analysis, the solar cells were characterized by QE and electroluminescence (EL) as described in [Ste+13c; Gei+13; Kir+08]. The short-wavelength artifact in the QE measurement caused by luminescent coupling was corrected by following the procedure shown in [Ste+13c]. EL has been used to: 1) calculate the subcell dark J-V curves

by using Rau's reciprocity theorem [Rau07] and following the procedure in [Gei+13; Gei+14]; 2) verify and confirm the LC results by using the subcell dark J-V curves and 3) analyze the structures at the subcell level in the presence of luminescent coupling [Gei+15b]. All characterization data were taken at nominal temperatures of 25, 50, 75, 100 and 120°C. A calibrated platinum-RTD surface probe was used to monitor the temperature on the stage surface. Therefore, every value shown in the upcoming graphs corresponds to the actual temperature on the stage. In order to control the cell temperature during the QE measurements, a Wavelength Electronics LFI-3751 controller was used. A gold-plated copper sample stage was mounted on a thermoelectric heater with a 10k Ω thermistor coupled to the copper block.

6.3.2 LC characterization procedure

In order to extract the luminescent coupling current and its related parameters, the short circuit current of the solar cell is measured as a function of the light intensity, as described in [SG12; Ste+13c]. Spectral conditions are varied to force the luminescent coupling current between the two junctions to dominate the limiting photocurrent. An adjustable light simulator comprising a Xenon lamp and high-brightness LEDs with wavelengths 470, 740 and 850-nm was used to construct the emulated spectrum to selectively vary the light intensity in the GaInP and GaAs subcells, respectively (see Fig. 6.3). For every data point, the intensity on each junction relative to the ASTM G173 direct solar spectrum (X_i or equivalent suns for junction i , where $i = 1$ corresponds to the top cell) was determined by measuring the photocurrent on a corresponding calibrated single junction reference cell, and correcting for any spectral mismatch using a spectral mismatch correction factor calculated using the measured light spectra and the quantum efficiency measurements [Ost+]. The relative intensity of each junction was characterized as each LED was varied, and any spectral overlap between the LEDs was accounted for. The LED overlap was observed to be stronger as the temperature is increased, for the particular LED and cell bandgaps used, due to the bandgap temperature dependence. However, this overlap is well captured by the reference cell characterization (as shown in the next section). As mentioned above, the LC current is measured by forcing the subcell under test to limit the tandem cell current in order to analyze the LC behavior. To force these conditions, the corresponding LED light source (X_1 or X_2 for a dual junction solar cell case) is varied for the subcell under test from zero to the full range of the LED power while the other subcells are under a fixed LED light power. The J_{sc} of the overall tandem cell is measured at every light bias step and the J_{sc} vs equivalent suns curve is obtained. A detailed description of the measurement technique can be found in [SG12; Ste+13c]. Regarding the EL measurements, we followed the procedure de-

Figure 6.3: Schematic of 1-sun adjustable simulator with Xenon lamp and various LEDs light sources. An example of the spectrum measured by the spectroradiometer is also depicted at the left part of the figure. The LEDs shown correspond to the configuration used in the LC characterization

scribed in [Rau07; Kir+08] using a high resolution spectroradiometer from Spectral Evolution (SR-3500). The EL spectrum is measured under a range of different forward current injections. EL also allows to deduce the external luminescent efficiency which is an important metric to measure the quality of solar cells and it is defined as the fraction of the total dark recombination current that leads to radiative recombination and emission of photons that escape out the front of the device [Gre12]. The external radiative efficiency is calculated by integrating over the measured EL peak emission spectrum (in units of current density) of the subcell and dividing it by the injected current. More details on the measurement procedure can be found in [Gei+13; Gei+14].

6.4 Luminescent coupling characterization results

The recognition and analysis of LC is a relatively new object of research that entails a possibility that the reader may not be entirely familiar with some of its evidence and manifestation. Therefore, we will briefly describe the most common observation of LC in multijunction solar cell characterization prior to show the LC results as a function of temperature.

A clear signature of luminescent coupling is typically encountered in QE measurements. For example, in a two-junction solar cell, a non-negligible spectral response in the range of the top junction is detected when measuring the second junction. This response is typically a

function of light bias applied to the top junction to avoid current limitation from this subcell. To illustrate this effect, Fig. 6.4 shows the spectral response of a dual-junction GaInP/GaAs solar cell (one of the devices studied in this chapter) as a function of the light bias in the top junction. As can be seen, the GaAs spectral response (green lines) in the region of the top junction absorption ($\lambda < 700$ nm) increases with the 470-nm LED power. Assuming the absence of a low breakdown voltage, a non-negligible QE in this range for GaAs may be attributed to different phenomena, namely: a) a low shunt resistance, b) incomplete absorption of the top cell and 3) LC effects [Meu+03; Lim+13; Bar+15a]. A low shunt resistance would imply a non-zero slope photo current generation of the GaAs subcell that is dependent on voltage bias. In this case, this is ruled out mainly because the same QE has been measured at different voltages, i.e. $-V_{oc}$ of the top cell and around 0V at the GaAs subcell. Moreover, the shunt effect tends to saturate with the LED light intensity. Incomplete absorption of the top cell can be also ruled out because the GaInP subcell is thick enough to absorb almost all light, specially at low-wavelengths (< 550 nm). The transmitted light reaching the 2nd junction is expected to be low, being unable to explain QEs above 10%. The GaAs QE dependence with light intensity shining the top junction can be explained by LC effects that affect the QE measurement of the device. The extra photocurrent that GaAs develops comes from the absorption of the GaInP radiative emission that increases when increasing the amount of light in this junction. Indeed, a higher spontaneous emission from GaInP is expected mainly because the quadratic dependence on the excess carrier density of radiative recombination. Accordingly, a strong LC effect with QE values above 30% is observed for the highest power used indicating the high material quality of the top junction. Interestingly, the GaAs QE at its absorption range ($\lambda > 700$ nm) decreases when increasing the light intensity. According to small signal analysis performed by Lim et al., the LC photocurrent has a negative polarity with respect to the photogenerated current of GaAs suppressing the QE output [Lim+13].

As mentioned above, other phenomena such as shunting conductance or low breakdown voltage complicate the detection of LC. However, both effects can often be avoided by setting appropriate voltage or light bias conditions to 1) ensure the subcell to be measured close to short circuit conditions and 2) ensure the current limitation in the subcell to be measured by applying enough amount of light on the others [Meu+03; Bar+15a]. Moreover, once the appropriate conditions are found, the spectral response is not a function of the light bias on the overdriven junction as LC is. Indeed, shunting conductance should decrease its appearance when light is increased.

It is important to note that the measurement artifact occurs because of the nature of QE

Figure 6.4: EQE of a GaInP/GaAs dual-junction solar cell for different 470-nm LED intensities without any LC correction procedure applied.

measurements of multijunction solar cells. Light bias conditions must be set properly to access specific subcells where strong current mismatch occurs. The GaAs response is not actually generated due to the external light rather than internal extra generation process. Indeed, this is not representative to the operation under a given spectrum. In this case, the response observed by LC in short-wavelengths (having implications in the long wavelength range as explained before) for GaAs would not occur because at those wavelengths almost all incident flux is being absorbed by the top cell. What is required is that the cell responds to the external light flux, i.e. monochromatic light. Accordingly, because the QE is commonly used to adjust the solar simulator spectrum there is a need to remove the LC effects. Therefore, procedures of LC correction in QE measurements were required for proper characterization of multijunction solar cells [Ste+13c; Shv+16]. One of the most known procedures has been developed by Steiner et al. and it is the one applied to the following results [Ste+13c].

6.4.1 QE results

Fig. 6.5a shows the EQE measurements for the GaInP/GaAs two-junction cell (ML732) as a function of temperature. As mentioned previously, all QE curves have been already corrected for LC effects on the measurements. As expected, a shift of the cut-off wavelength in the EQE of each subcell is observed due to the temperature dependence of the bandgap in each material. The reflectance (bottom of Fig. 6.5a) primarily shows differences with temperature

near the bandgap of the bottom junction. This indicates that the refractive index does not show significant changes at any measured temperature. The plateau of the EQE response also shows very little changes (less than 1-2%, which is within measurement uncertainty) indicating that the diffusion length is still greater than the cell thickness at high temperatures so as not to affect the carrier collection. Very similar behavior (6.5b) was found for the GaAs/GaInAs two-junction cell (MM708)

Figure 6.5: (a) EQE measurements (top) of the GaInP/GaAs two-junction cell and (b) the GaAs/GaInAs at different temperatures once corrected by luminescent coupling following the procedure described in [Ste+13c]. Reflectance of each solar cells is depicted at bottom figures of (a) and (b) at different temperatures

6.4.2 LC results

Two different measurements are carried out in order to analyze the luminescent coupling: 1) with background LED light illuminating the bottom junction at around one-sun, and 2) without any background LED light on the bottom junction. The use of both measurements provides a more reliable extraction of the LC parameters as well as the photocurrents of the subcells relative to standard test conditions. Fig. 6.6a and Fig. 6.6b show the measurements carried out to analyze the LC for GaInP/GaAs (ML732) and GaAs/GaInAs (MM708) cells as a function of temperature, for the cases with and without background light, and the fitting achieved by using the Steiner and Geisz model [SG12].

Figure 6.6: J_{SC} of GaInP/GaAs (a) and GaAs/GaInAs solar cell (b) at different temperatures for measurements (top) with background light X_2 , and (bottom) without the background light when X_1 is varied. Markers are data and lines are fits.

For GaInP/GaAs solar cell, the measurements with background light (X_1 varied and $X_2 \sim 0.9$ suns) show two different slopes as can be seen in the top graph of Fig. 6.6a (top). The first slope, on the left, corresponds to the top cell limiting the photocurrent until it reaches the background photocurrent generated by the bottom cell. At this point, the top cell is not limiting the current, so the limiting photocurrent corresponds to the bottom cell background photocurrent plus LC photocurrent. The bottom graph of Fig. 6.6a shows clearly the LC where the bottom cell is not illuminated (X_1 varied and $X_2 = 0$) and the LC dominates the photocurrent for the whole curve. As can be seen, the slope of the lines is reduced as temperature increases so the LC diminishes with temperature. Fig. 6.6b shows the radiative coupling from the GaAs top cell to the GaInAs bottom cell for the MM708 device. In the case with background LED light measurements (top graph in Fig. 6.6b, $X_2 \sim 0.75$), LED overlap is present. The first slope ends at lower illumination intensity as temperature increases due to the increasing overlap of the 940-nm LED on the top cell. As temperature increases, the absorption range of each subcell extends to longer wavelengths, thus the GaAs cell absorbs more light from the 940-nm LED and lower illumination is needed to make the bottom cell the limiting subcell. No major

impact is expected from the LED overlap in the extraction of the LC properties since the LED intensities has been previously characterized by using appropriate reference cells. Finally, for $X_2 = 0$ (bottom graph of Fig. 6.6b), the curves that the LC dominates the J_{sc} and decreases with temperature.

6.5 Luminescent coupling model and results

Originally, LC current was associated to be a linear function of the recombination current in a particular emitting junction. More recently, it has been demonstrated that the luminescent coupling current exhibits a non-linear behavior depending on the competition of non-radiative and radiative recombination mechanisms of the emitting junction [SG12]. The latter is the model that has been used to analyze the LC behavior. We include temperature dependences of the diode parameters and show that they can be used to model the behavior of LC as a function of temperature.

Using a two-diode model with ideality factors of $n = 1$ and $n = 2$ in the absence of series resistance, shunting and reverse breakdown, the LC as a function of the relative light intensity in each junction (X_i) can be characterized by two experimentally measurable parameters [SG12]: 1) the coupling efficiency, $\eta_{i,i+1}$ and 2) ϕ_i . The first parameter evaluates the strength of the coupling by including optical effects (ability of photons to escape out of the subcell, absorption in layers between subcells, etc.) and the ratio between radiative and non-radiative components of the diffusion recombination current in the subcell emitting light. In other words, it is a fraction of $J_{01} \exp(qV/kT)$. The second parameter (ϕ_i) evaluates the linearity of the LC with light intensity from the upper junction and is given by: $\phi_i = \frac{J_{02}}{2\sqrt{J_{01}}}$. Both parameters, $\eta_{i,i+1}$ and 2) ϕ_i , determine the luminescent coupling current, $J_{i,i+1}^{LC}$, in junction $i+1$ and is calculated by [SG12]:

$$J_{i,i+1}^{LC} = \eta_{i,i+1} \left[\sqrt{\phi_i^2 + J_{rec}} - \phi_i \right]^2 \quad 6.1$$

where J_{rec} is the recombination current density. Since J_{rec} is a function of the total photocurrent density (J_{Total}) in the device, its calculation depends on which cell is limiting the current. Since we are dealing with two-junction devices, the LC dominates when the second, lower bandgap junction is limiting the photocurrent in the device. Therefore, $J_{rec} = J_{ext1} - J_{ext2} - J_{12}^{LC}$ and Eq. 6.1 can be solved directly by using the externally induced photocurrents, J_{ext1} and J_{ext2} (previously characterized) on top and bottom junctions, respectively [SG12]:

$$J_{LC}^{12} = \frac{\eta_{12}}{1 + \eta_{12}}^2 \left[\sqrt{\phi_i^2 + (\eta_{12} + 1)(J_{ext1} - J_{ext2})} - \phi_i \right]^2 \quad 6.2$$

In order to extract the LC parameters ($\eta_{i,i+1}$ and ϕ_i) from the experimental data of Fig. 6.6a and Fig. 6.6b, the simplest case is setting $\phi_i = 0$, which means that the luminescent coupling current is a function of $\eta_{i,i+1}$ and J_{rec} and can be explained by a single diode model ($J_{02} = 0$). However, even though there are some cases where ϕ_i can be neglected (i.e. for a very high quality cell and at a fixed temperature), we expect that the saturation current densities from the standard two-diode model, J_{01} and J_{02} change differently with temperature. Therefore, ϕ_i will probably not remain constant with temperature and should be considered to be variable. On the other hand, the main uncertainty on the calculation of the LC parameters ($\eta_{i,i+1}$ and ϕ_i) as a function of temperature is that multiple pairs of values of these parameters are able to get very good data fittings to the experimental measurements (the goodness of fit was evaluated by Chi-square tests where $\chi^2 < 0.01$ in each corresponding curve). Because of the existence of multi-solutions of the data fitting process for both $\eta_{i,i+1}$ and ϕ_i , it is compulsory to validate at least one of these LC parameters in order to provide more confidence to the model consistency. Because ϕ_i depends on the so-called saturation current densities (J_{01} and J_{02}) of each subcell, it can be estimated by measurements. To validate ϕ_i , we proceed as follows: 1) EL(T) measurements are performed and the subcells dark I-V curves are extracted following [Kir+08], 2) We fit those curves to a two-diode model in order to estimate the saturation current densities. Then, $\phi_i(T)$ can be derived from the relationship between the saturation currents mentioned above. Accordingly, by assuming proportionality in the relation of $D_{n,p}/\tau_{n,p}^{-1}$ with temperature and using the temperature dependence of the intrinsic carrier concentration [Bar87]:

$$n_i^2 \propto T^3 \exp\left(\frac{-E_g}{kT}\right) \quad 6.3$$

J_{01} can be expressed as:

$$J_{01}(T) = q \left(\frac{D_{n,p}}{\tau_{n,p}^{-1}} \right)^{1/2} \left(\frac{n_i^2}{N_{D,A}} \right) = C_1 T^3 \exp\left(\frac{-E_g}{kT}\right) \quad 6.4$$

where C_1 is a proportionality constant, $D_{n,p}$ the diffusion length of holes or electrons, $\tau_{n,p}$ the carrier lifetime of holes or electrons, $N_{D,A}$ the doping level of acceptors or donors and the other variables have their usual meaning. Assuming: a) the trap energy level is equal to the intrinsic Fermi level, b) the capture cross sections are equal for both carriers ($\sigma = \sigma_n = \sigma_p$) and c) for $V \gg kT/q$, the temperature dependence of J_{02} arises from both n_i and that of the lifetimes through the thermal velocity (ν_{th}) [SN06]:

$$J_{02}(T) = \frac{qWn_i}{2}\sigma\nu_{th}N_t = C_2T^2 \exp\left(\frac{-E_g}{2kT}\right) \quad 6.5$$

where C_2 is a proportionality constant, W is the depletion width, N_t is the defects density and the other variables have their usual meaning. Finally, combining Eq. 6.4 and Eq. 6.5 and solving for ϕ_i yields:

$$\phi_i^2(T) \propto T \quad 6.6$$

Therefore, we proceed by using Eq. 6.6 to calculate the temperature dependence of ϕ_i and then we use these ϕ_i values as input data to calculate $\eta_{i,i+1}$. As a result, the LC parameters as a function of temperature are plotted in Fig. 6.7. The η_{12} decreases by just 11% from 25 to 75°C and by 45% from 25 to 120°C in the case of the GaInP/GaAs cell (ML732). In the case of the GaAs/GaInAs cell (MM708), η_{12} drops by 25% from 25 to 75°C and by 45% from the lowest to the highest temperature measured.

Figure 6.7: Luminescent coupling parameters: (a) η_{12} and (b) ϕ_1 fitted from the measurements for the GaInP/-GaAs cell, ML732 (blue region filled circles) and the GaAs/GaInAs cell, MM708 (red region and filled squares).

The possible values that the LC parameters that can be well fit to the experimental data are within the colored regions around the dotted curves. In order to calculate this uncertainty (colored regions), we establish three different pairs of values that achieve reasonable good data fittings. The black curves (1st pair of values) correspond to the best fitting while the colored regions correspond to possible values that the LC parameters can take within lower (2nd) and upper (3rd) limits where the χ^2 is closest to 0.01.

The black curve corresponding to η_{12} has $\pm 6\%$ of deviation for the GaInP/GaAs cell and around $\pm 10\%$ for the GaAs/GaInAs cell while ϕ_1 has a deviation of $\pm 35\%$ and $\pm 15\%$ for both cells, respectively. Fig. 6.7 shows that a lower uncertainty in η_{12} can be found for cases where

ϕ_1 is relatively low. In cases where ϕ_1 is low (as in the case of GaInP in the ML732 device), its variation is high ($\pm 35\%$) and it has a lower deviation impact on η_{12} ($\pm 6\%$). This impact on η_{12} increases ($\pm 10\%$) when ϕ_1 is higher even if its deviation is lower ($\pm 15\%$) as in the case of GaAs in the MM708 device. Therefore, a low ϕ_1 indicates a relatively small contribution from the space charge region (lower J_{02}) and η_{12} becomes the dominant parameter.

Despite the uncertainty, the trend of each parameter considering these deviations remains unchanged. For example, any value taken for ϕ_1 in the coloured region of each structure in Fig. 6.7b yields similar trends for η_{12} in Fig. 6.7a. Consequently, the use of ϕ_1 as an intermediate parameter in order to achieve robust values of η_{12} can be justified. In addition, as $\eta_{i,i+1}$ is the LC efficiency provides much more physical insight than ϕ_1 .

It should be mentioned that some other J_{02} temperature dependences such as $J_{02} \propto T^{5/2} \exp(-E_g/2kT)$ may be found in the literature [WNS77; RYH95; SB14; Bro+15]. Because the J_{02} parameter is related to the space charge recombination through defects, its temperature dependence is determined by the nature of those defects in each junction as well as by the bias conditions considered in its derivation. Therefore, it is reasonable to find different temperature dependences for J_{02} . If we consider the proportionality of J_{02} with $T^{5/2}$ then $\phi_1^2(T) \propto T^2$. Since ϕ_1 is a very sensitive parameter (no exponential dependence), this temperature dependence also leads to ϕ_1 values that lie between the ranges of values (coloured regions of Fig. 6.7) that achieve good data fittings to the experimental measurements of Fig. 6.6a and Fig. 6.6b.

6.6 Subcell material quality evaluation in the presence of luminescent coupling

6.6.1 Subcell analysis from dark IV models and internal voltages

A simplified two diode model has been used to analyze the behavior of each subcell as a function of temperature. This model is also useful to confirm the saturation currents employed for the calculation of $\phi_i(T)$. Since the cells have a very high quality (as shown by the presence of strong LC) and the EL measurements are not affected by series resistance in the measurement range, neither shunt nor series resistance were considered in the model. The recombination current at each subcell as a function of voltage and temperature can be expressed as:

$$J(V, T) = J_{01} \exp\left(\frac{qV}{kT}\right) + J_{02} \exp\left(\frac{qV}{2kT}\right) \quad 6.7$$

where J_{01} represents the saturation current densities at the quasi-neutral regions under low level injection conditions and includes radiative and non-radiative processes, J_{02} represents the saturation current density associated to the depletion and perimeter regions, the other variables have their usual meaning. The main dependence of the recombination current in the neutral regions on the applied voltage (V) is given by the dependence with the voltage of the injection of minority carriers from the depletion region into the neutral region (exponential dependence). Therefore, the ideality factor (n) in the first term of expression 6.7 is always 1 regardless of the predominant recombination mechanism in the neutral regions, radiative, Shockley-Read-Hall (SRH) or Auger. The recombination current in the depletion region is obtained by integrating the different recombination mechanisms (SRH, radiative, and Auger) rates along it. Usually, only the SRH recombination mechanism is considered in this region in the literature [LH10] because at forward bias capture processes are the major recombination-generation phenomena in the depletion region [SN06]. When the SRH recombination in the depletion region takes place through a single-level trap, assuming that the trap is located in the center of the band gap and the capture cross-section of electrons and holes are equal, the maximum value of the recombination occurs where the electron and hole densities are equal. In this case, the ideality factor n is 2. Though we have observed that in some cases this ideality factor can be lower than 2, in this work we assume it is 2 in accordance with the models for LC available at this moment. Extended models which include the possibility of using different ideality factors for the depletion region recombination current are under development and they will be used in future works³ [Gei+15b].

The dark J-V curves of the individual junctions of the tandem cells can be extracted from EL data to experimentally determine J_{01} and J_{02} . Errors in these EL results are reduced when the luminescent coupling is also considered [Gei+14]. An excellent agreement between the subcell dark J-V curves extracted from EL and the model has been achieved at each temperature. The saturation currents have been validated by comparing the saturation currents used to calculate $\phi_1(T)$ from Eq. 6.6 and the saturation currents extracted from the fits to the experimental dark J-V curves of each subcell as can be seen in Figs. 6.8 and 6.9.

Therefore, a proportionality factor for $\phi_1^2(T)$ can be extracted from Eq. 6.6 by using the

³At the time of writing this document, the extended models were already developed by Geisz et al., see [Gei+15b] for details

Figure 6.8: J_{01} and J_{02} for GaInP in the ML732 device. C_1 and C_2 (in units of mA/cm^2) correspond to the proportionality constants of Eqs. 6.4 and 6.5, respectively

saturation current values of Fig. 6.8 and Fig. 6.9, giving $1.85 \cdot 10^{-4} \text{ mA} \cdot \text{cm}^{-2} \text{K}$ for GaInP in the ML732 device and $6.34 \cdot 10^{-3} \text{ mA} \cdot \text{cm}^{-2} / \text{K}$ for GaAs in the MM708 device. The proportionality factor does not show a value that can be applicable to all materials. In fact, it is considerably higher for GaAs in the MM708 device indicating a high contribution from the J_2 term.

Figure 6.9: J_{01} and J_{02} for GaAs in the MM708 device. C_1 and C_2 (in units of mA/cm^2) correspond to the proportionality constants of Eqs. 6.4 and 6.5, respectively

Once the saturation currents values have been validated, they can be used to evaluate the quality of the subcells in each structure. We analyze two different curves as a function of temperature: 1) the bandgap-voltage offset under open circuit conditions, $W_{oc} = E_g/q - V_{oc}$ [Kin+11] and 2) the $V_{oc} - V_p$, where V_p corresponds to the parity voltage point where both the recombination current density in the quasi-neutral regions (J_1 , first term of Eq. 6.7) and in the

depletion and perimeter regions (J_2 , second term of Eq. 6.7) are equal [Hoh+13]. To base the model on realistic data, the V_{oc} and bandgap values of each material are extracted from the EL measurements. In Fig. 6.10 we plot the difference between the V_{oc} of the subcell at one sun and V_p and the bandgap-voltage offset.

Figure 6.10: Temperature dependence of W_{oc} and $V_{oc} - V_p$ for each top cell in the two structures analysed.

A positive $V_{oc} - V_p$ means that the recombination current density in the quasi-neutral regions starts to dominate before it reaches the V_{oc} of the subcell. A negative value means that the recombination at the depletion and perimeter regions is still strongly affecting the performance of the device at the V_{oc} point. This second case does not apply to any subcell analysed, as can be seen in Fig. 6.10. The higher the positive difference the lower the impact of the recombination at the space charge region and, thus, the better the quality of the subcell. The bandgap-voltage offset is similar in both cases. The W_{oc} decreases at a rate of -1.28 mV/K and -1.14 mV/K for the GaInP top cell in the ML732 and the GaAs in the MM708, respectively. This indicates that GaInP is most affected by temperature, but since $V_{oc} - V_p$ has a positive slope, it has lower influence of space charge recombination. This is consistent with having dominant J_{01} (as in the case of the GaInP in the ML732) over the J_{02} contribution to the total recombination current yield to higher temperature dependence ($J_{01} \propto T^3$) as shown in Eq. 4 and 5. The lower space charge recombination of the GaInP in the ML732 device can be attributed to the rear-heterojunction design. In the case of the GaAs in the MM708 device, the $V_{oc} - V_p$ is also positive but closer to zero and it remains almost constant with temperature indicating that at any temperature the space charge region recombination still limits the performance of the device.

6.6.2 Subcell internal radiative efficiency dependence on the injected current and temperature

The LC parameters are complementary and incorrect conclusions can be drawn if the LC is evaluated by looking at them individually. In fact, in section 6.5, we have shown higher coupling efficiency factors for GaAs (MM708), but having higher coupling efficiency factor does not necessarily mean better luminescent properties (η_{12} depends also on the optical properties of the semiconductor structure). Therefore, the behavior of the internal radiative efficiency with injected current and temperature is used to provide more insight and to evaluate the luminescent properties of the junction materials. The internal radiative efficiency is defined as the fraction of recombination events that are radiative and is one of the most important metrics to determine the quality of the solar cells [Gre12]. In order to calculate it, we use the optical modelling described in [Ste+13a]. This modelling is capable of computing average internal probabilities of an emitted photon to be re-absorbed in the junction ($\overline{P_{abs}}$) and to escape out of the front surface of the device ($\overline{P_{esc}}$). η_{int} can be defined from the optical modelling as:

$$\eta_{int} = \frac{\eta_{ext}}{\eta_{ext} - \overline{P_{abs}} + \overline{P_{esc}}} \quad 6.8$$

where η_{ext} is the external radiative efficiency, which is determined from EL measurements. The external radiative efficiency is defined as $\eta_{ext} = (J_i^{em})/(J_i^{inj})$, where J_i^{em} is the total external radiative flux from the i th junction in units of current density and is calculated by integrating over the EL peak emission spectrum and J_i^{inj} is the injected current density applied to the cell in the EL measurement. $\overline{P_{esc}}$ and $\overline{P_{abs}}$ are complicated functions of the geometry and the angle and wavelength dependent Fresnel coefficients at the front and back of the structure. Their expressions are given in Ref. [Ste+13a]. To accurately determine η_{int} , reliable refractive indices are needed. We have no measured data available for the extinction coefficient (k) of the materials involved for temperatures above 25°C. It was calculated by using the approach from [Pan71] where the k drops with the square root of the bandgap energy. The real part of the refractive index has been extended by extrapolating the measured indices with parameters of the well-known Sellmeier equation able to reproduce the last region (long wavelengths) of the refractive index of interest. The validation of this optical data has been performed by fitting the measured reflectance and QE response (not shown), reaching a satisfactory result.

The determination of $\overline{P_{esc}}$ (1.26% and 0.6% at 25°C for ML732 and MM708, respectively) and $\overline{P_{abs}}$ (73% and 84.2% at 25°C for ML732 and MM708, respectively) as a function of temperature does not show any significant changes, within 0.1% and 3-4%, respectively from 25°C

to 120°C for each top cell examined. It is reasonable to expect $\overline{P_{abs}}$ and $\overline{P_{esc}}$ to remain almost unchanged in the temperature range analysed since the QE and reflectance does not show any significant changes except at the bandgap regions (see Fig. 6.5a and Fig. 6.5b). Therefore, the variation in η_{int} is dominated by the variation in η_{ext} . Fig. 6.11 shows contour plots of the $\eta_{int}(J, T)$ for the subcells emitting light in each device (GaInP for the ML732 and GaAs for the MM708 device), as calculated from Eq. 6.8 and using EL data measured earlier. As can be seen in figure 6.11a, we find a dominant radiative component for the GaInP (high values of η_{int} even at low currents). $\eta_{int}(J, T)$ increases with the injected current, but it exhibits a strong reduction with temperature.

Figure 6.11: Contour plot of $\eta_{int}(J, T)$ of the top cells: (a) GaInP in ML732 (b) and GaAs in MM708

For the GaAs top cell in Fig. 6.11b, $\eta_{int}(J, T)$ also decreases with temperature, but at a lower rate than the GaInP top cell for any range of injected current. The higher sensitivity to the injected current suggests that at lower currents, the GaAs is still affected by a strong non-radiative recombination which decreases at higher currents. It is noteworthy that at high current densities ($\sim 86 \text{ mA/cm}^2$ or ~ 7 suns) and at any temperature below 100°C, the GaAs subcell has very high values of $\eta_{int}(J, T)$ that exceed 90%. The internal emission intensity shown in Fig. 6.11 can be affected by several mechanisms such as: non-radiative recombination via deep level defects, surface recombination, potential losses in heterostructure barriers, optical losses at the interfaces, cladding layers and tunnel junctions, etc. The temperature dependence of these processes is not a straightforward calculation. However, all those mechanisms can be included in the radiative and non-radiative lifetimes: τ_r and τ_{nr} . Accordingly, the internal radiative efficiency can be also defined in terms of the radiative and non-radiative lifetimes [Sch06]:

$$\eta_{int} = \frac{\tau_r^{-1}}{\tau_r^{-1} + \tau_{nr}^{-1}} \quad 6.9$$

The temperature dependences of τ_r and τ_{nr} are well-known and can be introduced into Eq.

6.9. From the bimolecular expression of radiative transitions, the B radiative coefficient has weak temperature dependence: $\propto T^{-\frac{3}{2}}$ [Sch06]. The dependence of the radiative lifetime is inversely proportional to B for a specific doping level. In the case of the non-radiative recombination lifetime (the Auger recombination is neglected), the temperature dependence is stronger: $\tau_{nr}^{-1} \propto \exp(-E_a/kT)$ [Sch06]. By combining the temperature dependences of the lifetimes into Eq. 6.9, a simple equation for the temperature dependence of the η_{int} can be expressed as:

$$\eta_{int}(T) = \frac{\tau_{r,T_0}^{-1} \left(\frac{T}{T_0}\right)^{-3/2}}{\tau_{r,T_0}^{-1} \left(\frac{T}{T_0}\right)^{-3/2} + \tau_{nr,T_0}^{-1} \exp\left(\frac{-E_a}{kT} + \frac{E_a}{kT_0}\right)} \quad 6.10$$

where T_0 corresponds to a given reference temperature, in this case we use 300K, and E_a is the activation energy of the trap. The exponential dependence of the non-radiative recombination is much stronger than the power law dependence, so the reduction of η_{int} is due to a decrease in the non-radiative lifetime. In Fig. 6.12, we show the values of η_{int} at one sun-equivalent injected current as obtained from the optical modelling and the fitting to equation 6.10. The trend can

Figure 6.12: Internal radiative efficiencies at one sun-equivalent injected current calculated by optical modelling described in [Ste+13a]. Dashed lines are the corresponding fitting curves calculated with Eq. 6.10

be explained by using Eq. 6.3 in all materials. As mentioned before, since the exponential behavior of the non-radiative lifetime has stronger temperature dependence than the radiative lifetime which follows a power law; the changes on the non-radiative lifetime values dominate the reduction of η_{int} as a function of the temperature. In fact, the τ_{nr} is more than one order of magnitude lower at 120°C than at 25°C while the τ_r increases slightly with temperature.

The activation energy is the most important parameter in predicting the trend of the curve. The lower the activation energy the lower the temperature dependence on the reduction of the internal radiative efficiency. Interestingly, the ratio $\frac{\tau_{r,T_0}^{-1}}{\tau_{nr,T_0}^{-1}}$ shown in Table 1 indicates that the effective carrier lifetime is dominated by the radiative lifetime at the reference temperature in both materials, being more dominant for the GaInP.

Table 6.1: Fitting parameters of Eq. 6.10

Junction	Structure	$\frac{\tau_{r,T_0}^{-1}}{\tau_{nr,T_0}^{-1}}$	E_a (meV)
GaInP	ML732	0.086	196 ± 14
GaAs	MM708	0.115	97 ± 14

6.7 Summary and conclusions

The temperature dependence on the luminescent coupling of multi-junction solar cells has been studied in two tandem solar cells (GaInP/GaAs and GaAs/GaInAs) that are components of an inverted metamorphic triple junction solar cell. The study has been carried out by means of LC analysis, dark and optical modelling. LC models have shown suitability for the analysis of the temperature impact on the luminescent coupling. This analysis showed that the luminescent coupling efficiency factor is reduced with temperature from test temperature to typical operating point (75°C) by 11% and 25% for GaInP and GaAs, respectively. From optical modelling, the luminescent properties of GaInP and GaAs subcells as a function of temperature and injected currents have also been studied. In the case of GaInP, it shows a high internal radiative efficiency even at low current densities, but it is strongly affected by the temperature which can be attributed to the dominant J_{01} in accordance with dark modelling. The internal radiative efficiency of the GaAs top cell performs better with temperature and reaches very high values at moderate injected currents. The low values of internal radiative efficiency of this GaAs top cell at low current densities suggest a strong non-radiative recombination component. In both materials, there is strong potential to mitigate the effect of temperature by exploiting the luminescent coupling properties at high currents densities or light concentration levels.

Future works

1. Incorporation of models for photon recycling. This can be done through the spontaneous photon emission calculation along the structure depending on the quasi-Fermi level separation. Once this quantity is obtained, the light travelling along a 1D or 2D structure must be calculated in order to provide an additional generation term that can be directly included into the continuity equation to be solved self-consistently. This will be a key factor to accurately model the performance of IMM structures being now developed in our Laboratory. These solar cells include efficient back reflectors that enhances photon recycling.
2. Incorporation of models for luminescent coupling between subcells for multijunction structures. Some part of the photon emission from radiative recombination in a specific junction can be absorbed by junctions underneath rather to be re-absorbed in the same junction.
3. Extension of the optical models to deal with full or partial incoherent behaviour of light. This will be important for multijunction structures where incoherent effects are important (e.g., mechanical stack III-V on Si, among others).
4. Incorporation of models to deal with free-carrier absorption effects. This will be useful for optimizations of germanium solar cells by considering different doping concentrations as well as back reflectors.
5. Implementation of transfer matrix method for 3D simulations.

6. Development of a simulation tool including TCAD modelling and distributed models (circuit simulators) in order to take advantage of each simulation tool.

APPENDIX A

Material parameters

The equations described in Chapter 2 are used to solve the main dependent variables such as ψ , n , and p . These equations also require the parameters which are specific to material properties. These parameters are, among others, the effective mass, bandgap, band offsets, carrier mobilities and relative permittivity. Furthermore, in order to calculate generation and recombination terms, some other parameters such as optical constants, recombination lifetimes (Auger, SRH and radiative) must be provided. Accordingly, in this Appendix, a review of the material parameters required for the simulation of multijunction solar cells is presented. Literature values and those not available in the literature but extracted by data fitting (as described in section 2.13.4) will be included. In addition, the models used for the calculation of the material parameters as a function, for instance, of doping concentration are also provided explicitly or by citing the corresponding reference.

First, the carrier transport properties (lifetime, mobility and diffusion length) of most of the materials simulated are presented. Then, we include a summary of the rest of parameters, namely: band parameters, recombination coefficients, band offsets, refractive indices, etc. The GaNAsSb material parameters are presented separately.

A.1 Carrier lifetime, mobility and diffusion length

Injection dependence is not explicitly included into the simulations. This means that minority carrier lifetime is not dependent on the free carrier density. This is typically observed for example in germanium, silicon, gallium arsenide, among others. Physically, at high carrier densities, the role of defect density gets lowered because of trap saturation effects that may result in higher minority carrier lifetimes at high injection conditions. For instance, this has been observed in measurements of the carrier lifetime in germanium [GV06]. In the case of III-V semiconductors that are typically measured by TRPL, the carrier lifetime tends to increase with the laser intensity as well [Lus09; Wal+16]. This may be attributed to a trap filling effect and to the strength of photon recycling [Bla62]. It may be expected in very high material quality that radiative recombination becomes the limiting mechanism. In such cases, high injection effects on the effective non-radiative carrier lifetime (due to trap-filling) may reduce its influence. This is not the case of germanium, where most of them are SRH-limited in a wide operation conditions (thousands of suns). All in all, more accurate modelling would be achieved by considering minority carrier lifetimes dependent on the free carrier density.

In order to have access to minority carrier transport properties, several characterization techniques are usually required to provide a higher degree of confidence. Minority carrier lifetimes in III-V semiconductors are typically measured by TRPL¹ while diffusion length may be extracted from electron beam-induced current (EBIC) or transport imaging (see for instance [Hae+09; Max+13; Hae+14; Nie+17]). Then, minority carrier mobility is deduced from these two quantities. The use of other techniques such as DLTS is not typically reported probably because the high quality of III-V materials exhibit low trap densities that may be below the detection level of DLTS. In this section, a literature review of the minority carrier transport properties for most of the materials used in the simulations is presented. Literature for GaAs has already gathered full consensus as well as for germanium. For the case of GaInP, the literature is scarcer and due to the local atomic ordering of this material, transport anisotropy has been reported increasing the complexity for accurate extraction of such properties [Hae+14]. GaNAsSb is reported separately.

¹TRPL data must be analysed carefully mainly because carrier lifetime is usually injection level-dependent.

A.1.1 GaInP

Fig. A.1 summarizes minority carrier lifetimes measured by TRPL and the ones deduced from our data fitting.

Figure A.1: Minority carrier lifetime found in literature (symbols) for p-type samples (no data found for n-type). Haegel data (low level injection conditions) shows annealed and as-grown MBE-samples (A, AG, respectively) [Hae+14]. Dagan et al. [Dag+16] and Perl et al. [Per+17] (low level injection conditions) are MOVPE-samples. Schultes et al. data is for MBE-samples and doping values between $10^{15} - 10^{16} \text{ cm}^{-3}$ are estimated (UID samples). The high values from Dagan et al. suggest that measurements were performed possibly in high injection conditions. Since our GaInP solar cells are clearly dominated by SRH, the effective lifetime would be very similar to that of SRH one.

Fig. A.2 summarizes the majority and minority carrier mobilities found in the literature.

Figure A.2: Majority and minority carrier mobilities found in literature (symbols) and the ones calculated by using Sotoodeh equations (lines) [Sot+00]. Haegel et al. is for MBE-grown GaInP [Hae+14] measured in two different crystallographic orientations. Jakomin et al. data is taken from [Jak+12].

A.1.2 GaAs

Fig. A.3 shows the SRH-lifetime as a function of doping concentration for minority electrons and holes. The fitting parameters for SRH-lifetime were taken from Lumb et al. (see [Lum+14] and references therein). The B radiative coefficient used in all fits ranges between $1 - 2 \cdot 10^{-10}$ cm³/s which are in the range of what is deduced for upright solar cell grown on-substrate (see [Ste+13b] and references therein).

Figure A.3: Minority carrier lifetime (SRH) found in literature (symbols). Figure adapted from Lumb et al. [Lum+14] (see references therein for experimental data). Lines calculated by using Eqs. and fitting parameters also from Lumb et al. [Lum+14].

Fig. A.3 also suggests that n-type absorbers would exhibit higher material quality (thus V_{oc}) than traditional p-type ones, but the main limiting mechanism (unless BSR is used) is the diffusion length because of the lower minority hole mobility as depicted in Fig. A.4.

Indeed, n-type absorbers have demonstrated very high material quality and efficiency values practically equal to record solar cells [Ste+13a; Hwa+16; Kay+11]. For those cases, diffusion length was not an issue because of the use of back reflectors (substrate removed), but for cases on-substrate, Bauhuis et al. showed that diffusion length was the limiting mechanism to achieve comparable photocurrent than record cells. On-substrate devices still exhibited higher open circuit voltage for n-type absorbers over the p-type ones [Bau+16] consistent with Figs. A.3 and A.4.

Figure A.4: Electron (left) and hole (right) mobilities for n-type and p-type GaAs. Niemeyer, Tiwari, Lundstrom, Sotoodeh and Lovejoy data are taken from [Nie+17], [TW90], [Lun+90], [Sot+00] and [Lov+92], respectively. Input model lines were calculated by following the equations from [AD97].

A.1.3 Ge

The germanium effective bulk minority carrier lifetime follows the well-known phenomenological expression [GV06]:

$$\tau_{bulk} = \frac{\tau_{SRH}}{1 + \left(\frac{n_{dop}}{n_{thr}}\right)} \quad \text{A.1}$$

where n_{thr} is a reference threshold doping concentration and τ_{SRH} is mainly a function of doping concentration, injection level and trap characteristics (detailed equation and parameters are found in [Gau+07]). Fig. A.5 shows most of the experimental data found in the literature and the calculations following expression for different carrier densities (n_{ex}), thus injection levels ($k = n_{ex}/n_{dop}$).

Mobilities are calculated via:

$$\mu = \frac{\mu_l}{1 + \left(\frac{N}{N_{ref}}\right)^\gamma} \quad \text{A.2}$$

where N is the doping concentration, γ and N_{ref} are adjustable parameters and μ_l for both electrons and holes is taken from [Pri53]. Fig. A.6 shows the minority carrier mobility as a function of doping concentration for electrons and holes. The calculated values by using Eq. A.2 (lines) are consistent with those estimated by Prince [Pri53] and Yoon et al. [Yoo+05].

Diffusion length as a function of doping concentration was calculated by using Einstein

Figure A.5: Carrier lifetime found in literature for n-type (filled symbols) and p-type Ge (empty symbols). See Gaubas et al. and references therein [Gau+07] for the parameters used in these calculations (Eq. A.1). Lines show the calculated values by solving the analytical equations taken from [GV06] for different excitation levels. Dashed lines correspond to the values with $k \geq 1$. This figure is adapted from [GV06] and updated including Yoon et al. data for commercially available Ge material for solar cells [Yoo+05].

Figure A.6: Calculated minority carrier mobility for n-type and p-type germanium and experimental data taken from [Yoo+05]. $\gamma = 0.55$ and $\gamma = 0.58$, $\mu_l = 1900$ and $\mu_l = 3900$ and $N_{ref} = 7 \cdot 10^{16} \text{ cm}^{-3}$ and $N_{ref} = 10^{17} \text{ cm}^{-3}$ for n-type and p-type, respectively.

relation and the effective carrier lifetime. The effective carrier lifetime was estimated by using data from Fig. A.5, Auger and radiative coefficients presented in Table A.6 and mobilities from Fig. A.6. Fig. A.7 shows the minority carrier diffusion length for p-type and n-type germanium as a function of the doping concentration including the available experimental data found in the literature as well as the estimated values from data fitting (p-type). For data fitting, mobility was fixed and SRH carrier lifetime varied according to Eq. A.1.

Figure A.7: Minority carrier diffusion length as a function of doping concentration considering the effective carrier lifetime (Auger, SRH and radiative components).

Minority carrier properties for p-type germanium are consistent with those found in literature. Friedman et al. reported internal quantum efficiencies very similar to the ones developed here (very similar to the #A3 sample shown in Section 3.4.2 in the IR range where the base is the only contributor to the QE) [FO01]. For such samples, Friedman et al. deduced a $L_D \sim 30\mu m$ which is similar to the one deduced here ($L_D = 28\mu m$, being aware of the nominal doping concentration difference). Interestingly, the L_D deduced in our samples ($N_A = 10^{18} \text{ cm}^{-3}$) seem to be higher than those previously reported (asterisks shifted to the right). Carrier concentration was also measured by electrochemical capacitance voltage (ECV) and secondary ion mass spectrometry (SIMS) in our case, suggesting a possible higher material quality for the p-type substrates. This discrepancy may be either due to higher material quality, but also due to the fact of the strong dependence of carrier lifetime with injection level. If higher material quality is observed in the current substrates, it will not appear as a V_{oc} enhancement (very similar in our case and those reported by Friedman et al.) mainly because germanium single junction solar cells are typically emitter-limited (either by interface or bulk recombination). All in all, the use of the simple equations shown here seems to work fine, at least in the limited doping range tested here. In the case of the n-type material, it is more complex to test the values shown in Figs. A.5 to A.7 because of the high impact of thermal load and growth conditions, the non-uniform doping profile as well as the lack of data. A more detailed study of n-type emitters was presented in Section 3.4.

A.1.4 AlGaInP, AlInP and AlGaAs

AlGaInP, AlInP and AlGaAs lattice matched to GaAs have been used as *inactive* layers² (window, BSF or at tunnel junctions). The minority carrier properties of these layers are less critical to be accurately known than those of materials forming the p-n junction itself and depending on the design. In fact, the photogeneration that typically reaches the BSF is low and its contribution to the photocurrent is usually negligible. The carrier collection of the window layer is assumed to be poor, so it will not contribute significantly to the overall photocurrent. For instance, for the top cell window layer (i.e., AlInP), the low collection properties at this layer can be attributed to: a) surface recombination and b) a presumable low diffusion length of minority carriers due to the high aluminium content (53%) and the related oxygen incorporation that may be associated to deep level traps [NTA86; Sto+99; Hec+13; Vai+16]. Hence, minority carrier lifetimes are typically fixed to constant values (extracted from QE data fitting) in all simulations.

The carrier mobility instead deserves to be mentioned for the AlInP material. The majority carrier mobility dependence on the doping level may have an important impact since it affects directly the conductivity of this layer where lateral current flow could take place (see Section 4.3 for a case study). In such cases, an extrapolation is carried out departing from majority carrier mobilities for n-type AlInP (lattice matched to GaAs) found in literature (for $N_D < 10^{19} \text{ cm}^{-3}$) [KF97; Gud+08; Dai+15]. Here, we use a simple impurity-dependent mobility expression able to fit the data from literature and extrapolate it to higher doping levels [Hil74]:

$$\mu_n = \frac{\mu_l}{1 + \left(\frac{N_D}{N_{ref}}\right)} \quad \text{A.3}$$

where μ_l is the mobility limit due to lattice scattering processes, N_D is the doping level and N_{ref} is an arbitrary reference doping density which equals $4 \cdot 10^{16} \text{ cm}^{-3}$. The ratio between these two doping concentrations relates the impurity scattering affecting the effective mobility of carriers. We estimate μ_l from the following equation for $(\text{Al}_x\text{Ga}_{1-x})_{0.53}\text{In}_{0.47}\text{P}$ quaternary alloy [Ada09]:

$$\mu_l(x) = 4300 - 6000x + 3000x^2 \quad \text{A.4}$$

where $x=1$ for AlInP. The μ_n values published in literature [KF97; Gud+08; Dai+15] together with the fit obtained with eq. A.3 are shown in Fig. A.8.

²Although its low minority carrier properties, the window layer typically contributes slightly to the carrier collection in any III-V solar cell. The AlGaAs material has only been used as BSF or at tunnel junctions

Figure A.8: Majority electron mobility in AlInP lattice matched to GaAs taken from [Gud+08; KF97] (empty symbols) and [Dai+15] (which corresponds to MBE-grown samples, filled symbols). Solid line corresponds to the values calculated from Equation A.3.

Measured Hall mobilities for both p-type and n-type AlGaInP p-type and n-type can be found in [IK89; Bou93; Ada09] and references therein. For AlGaAs, carrier mobilities were taken from [LRS96].

A.2 GaNAsSb

The GaNAsSb (1 eV) is a relatively novel material so literature is not extensive regarding its optical and electronic properties. Moreover, the photovoltaic, electrical and optical properties which are very dependent on the growth conditions and post-growth thermal treatments [Har+02; Har+07; Tan+11]. Therefore, there was a need to determine the main properties of the GaNAsSb material studied in this thesis in Chapter 5.

In order to obtain some of those properties of the GaNAsSb material, several characterization techniques have been performed³ such as: variable-angle spectroscopic ellipsometry (VASE) (shown in Section A.4), Hall measurements and TRPL, among others. The following table shows the main parameters required and the corresponding method of determination.

³Most of the GaNAsSb characterization presented in this section was performed by L. Ayllón and also by E. Ochoa and M. Gabás (UMA).

Table A.1: Summary of characterization techniques used in this thesis to obtain the main material parameters of GaNAsSb as well as the theoretical method of extraction.

	Parameter	Extraction from
Band parameters	Bandgap	QE, PR, T...
	Dielectric permittivity	Interpolation [VM03]
	Density of states	Interpolation [VM03]
	Effective masses	Interpolation [VM03]
	Band discontinuity	[Yue06]
Optical	Refractive index $n(\lambda), \alpha(\lambda)$	VASE
Electrical	Carrier mobility	Hall
	Carrier lifetime	TRPL

A.2.1 Hall Mobility

Hall measurements were carried out for several samples (n-type and p-type) with different doping concentrations which are summarized in Table A.2.

Table A.2: Carrier concentrations measured by ECV and majority carrier mobilities measured by Hall for a set of GaNAsSb samples with different nominal doping concentrations and dopant types.

Device	Polarity	Doping concentration (cm ⁻³)			μ (cm ² /V.s)
		Nominal	Hall	ECV	
N2903	p-type	1·10 ¹⁷	1.3·10 ¹⁷	-	72
N2904	p-type	5·10 ¹⁷	3.8·10 ¹⁷	5·10 ¹⁷	69
N2905	p-type	1·10 ¹⁸	7.7·10 ¹⁷	8·10 ¹⁷	64
N2906	n-type	1·10 ¹⁷	1.2·10 ¹⁷	7·10 ¹⁷	266
N2907	n-type	5·10 ¹⁷	1.05·10 ¹⁷	7·10 ¹⁷	128
N2908	n-type	1·10 ¹⁸	-	-	-

A.2.2 Carrier lifetime and diffusion length

A surface recombination velocity between GaNAsSb/GaAs of $2 \cdot 10^3$ cm/s has been also extracted by TRPL⁴.

Figure A.9: Minority carrier lifetime measured by TRPL in DH for p-type and n-type GaNAsSb (1 eV) samples and assuming nominal — or typical for UID samples — doping concentrations. Doping and τ_{SRH} values deduced from GaNAsSb single junction solar cell structures by multiple data-fitting (QE and V_{oc} , see section 5.3.2) are also depicted (triangles).

Diffusion lengths for holes in GaInNAs (1eV) of about $0.9 \mu m$ have been reported in MOCVD samples [GF02]. Electron diffusion length grown by MBE has shown higher values than the ones in MOCVD ($0.5 \mu m$) which is similar to this work (see for instance [Har+05; Kur+00]) while diffusion length for record solar cells [Jon+13] and recent works [MAO16b] suggest values above $1 \mu m$ (our estimations). The maximum electron diffusion length from the samples studied here (suggested by QE data fitting) is 160 nm.

A.3 Band offsets

Many of material systems used in typical lattice-matched multijunction solar cell structures are currently being used also for the fabrication of visible light-emitting devices, heterojunction bipolar transistors and MOSFET applications. One of the most important information needed to understand semiconductor devices that involves heterointerfaces is the band alignment between two different semiconductors. This information may be estimated by different indirect

⁴Data provided by the Quantum Photovoltaics group at Imperial College London.

methods. Some of the experimental techniques include: C-V profiling, internal photoemission, photorefectance, XPS and analysis of 2D electron gases, among others.

All band alignments for any heterojunction were considered to be Type I. A summary of the band offsets of most heterojunctions is presented in Table 4.3. Regarding GaNAsSb/GaAs band offsets, a thoroughly characterization has been carried out by Yuen et al. [Yue06]. For cases where no literature data is available Anderson's rule has been applied.

A.4 Refractive indices

The knowledge of the optical properties of all materials involved in multijunction solar cells is of paramount importance for their development. In fact, analytical models [Hov75] and drift-diffusion simulators typically used to predict solar cell performance require reliable optical constants (wavelength dependent refractive index and absorption coefficient) of the materials to improve their accuracy [Coi+11].

Besides the obvious critical importance in knowing the optical constants of materials involved in the p-n junction, the role of *inactive* layers on light transmission to the underlying layers is not negligible. For instance, AlInP, AlGaInP, GaInP and AlGaAs are usually employed as passivating and barrier layers in III-V solar cells, namely, front/back surface fields, tunnel junctions and buffer or nucleation layers with thicknesses ranging from tenths to hundreds of nanometers and up to the micrometer range (i.e. as in compositionally graded buffer layers in metamorphic structures). In the case of III-V arsenides such as GaAs and AlGaAs (see [Bla82; Pal97; Pal85] and references therein) and germanium (see [Pot85; NSM15] and references therein) are well studied and significant amount of optical information can be found in literature. The optical properties of III-V phosphides alloys with full Al-compositions have been already reported [Lee+93; Kat+94; Ada+94; DeL+95; Sch+95; Als+97; Fer+02], however, it is well known that the electrical and optical properties of solar cells are dependent on the growth conditions (temperature, V/III ratio, growth rate, annealing for dilute nitrides [Ben+10a], etc.), doping concentration and dopant type. Moreover, the samples are not usually studied as a function of doping concentration which is typically found in solar cell structures.

Accordingly, here we present a summary of the optical constants data taken from the literature as well as the ones obtained by VASE of several III-V materials (see for instance [Och+18] and references therein for III-V phosphides) including dilute nitrides. Figs. A.10 and A.11 summarizes the real and complex refractive index of all materials used in this thesis. A reference list for each material is listed in section A.5.5.

Figure A.10: Real part of refractive index for several III-V materials as well as GaNAsSb and germanium. GaInP(o) stands for partially-ordered GaInP while GaInP(d) stands for disordered GaInP.

Figure A.11: Extinction coefficient for several III-V materials as well as GaNAsSb and germanium. GaInP(o) stands for partially-ordered GaInP while GaInP(d) stands for disordered GaInP.

A.5 Summary of material parameters and models

A.5.1 Mobility

The carrier mobility details are found in section A.1. The parameters for the saturation velocity were taken from built-in model included in Atlas [Sil16]. Saturation velocities for GaInP (and AlGaInP) can be found in [SNN99; HHF00; AKC09; Liu+93; YHD02].

A.5.2 BGN

Bandgap narrowing has been applied to GaAs (p-type) and Ge (n-type and p-type) [JR91], AlGaAs [LRS96] and GaAs (n-type)[Luo+02]. In the case of phosphides due to the uncertainty on the effects of BGN and ordering parameter, BGN has not been included.

A.5.3 Interface recombination

Important interface recombination was required to be set typically at the interface between window/emitter. For the case of AlInP/GaInP interface recombination velocity (IRV) was below 1000 cm/s while for the case of GaInP/GaAs $IRV < 3000$ cm/s. For germanium, see Section 3.4. Surface recombination velocity (SRV) was by default assumed to be *infinite* (i.e., $SRV \gg v_{th}$) in any case unless specified in the text.

A.5.4 Tunnel junction parameters

Table A.3 summarizes the tunneling parameters for the two tunnel junctions analysed through this thesis.

Table A.3: Tunneling parameters for non local band to band tunnel models and trap-assisted tunneling

Material	AlGaAs/GaInP	AlGaAs/GaAs
m_{TAT}	0.01	0.01
m_e^{NLBBT}	0.026/0.0875	0.07/0.067
m_h^{NLBBT}	0.63/0.7	0.7/0.67

A.5.5 General material parameters

Table A.4: Summary of semiconductor material parameters used for simulations of the main layers of GaInP solar cells.

	Materials			
	Al _{0.53} In _{0.47} P	Ga _{0.51} In _{0.49} P	Ga _{0.51} In _{0.49} P	(Al _{0.2} Ga _{0.8}) _{0.5} In _{0.5} P
Region	Window	Emitter	Base	BSF
Band parameters ^a				
ϵ	11.7	11.8	11.8	12.7
E_g (eV)	2.35	1.8:1.9	1.8:1.9	2.03
N_C (cm ⁻³)	1.4·10 ¹⁹	6.24·10 ¹⁷	6.24·10 ¹⁷	1.96·10 ¹⁸
N_V (cm ⁻³)	1.37·10 ¹⁹	1.46·10 ¹⁹	1.46·10 ¹⁹	1.25·10 ¹⁹
n_i (cm ⁻³)	0.256	2.37·10 ³ :343	2.37·10 ³ :343	23
Effective masses				
m_n^*/m_0	0.35 ^b	0.088 ^c	0.088 ^c	0.11 ^d
m_p^*/m_0	0.67 ^b	0.695 ^c	0.695 ^c	0.63 ^d
Band offsets				
ΔE_V	0.57 · ΔE_g		0.57 · ΔE_g	
$\Delta E_C : \Delta E_V$	52:48, 67:33 ^e		43:57 ^e	
Recombination Parameters ^a				
C_n (cm ⁶ /s)	10 ⁻³⁰	4.7 · 10 ⁻³⁰	4.7 · 10 ⁻³⁰	10 ⁻³⁰
C_p (cm ⁶ /s)	10 ⁻³⁰	1.1 · 10 ⁻³⁰	1.1 · 10 ⁻³⁰	10 ⁻³⁰
B (cm ³ /s)	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻¹⁰	10 ⁻¹⁰
τ_p (ns)	10 ⁻⁴	See Section A.1.1	See Section A.1.1	1
τ_n (ns)	10 ⁻⁴	See Section A.1.1	See Section A.1.1	1
Optical constants				
n,k	In-house ^f	In-house ^f	In-house ^f	In-house ^f

^a Most from [LRS96] and [VMR01]. For electron affinity see also [Jia+06] and references therein. For AlInP and AlGaInP, N_C and N_V were calculated from their effective masses.

^b From [Bou93]. Different values may be found in [Kuo+97; Ada09] (e.g., $m_e^* = 0.12$).

^c From [LRS96]. Different values may be found in literature. Moreover, they may be dependent on the ordering parameter [ZS91; VMR01; Ada09].

^d From [Bou93]. Different values may be found in [Ada09; Kuo+97] (e.g., $m_e^* = 0.14$).

^e From [Ada09]. See also [Bou93]. For AlGaInP/GaAs see [Yi+09; WO87] and references therein for all aluminium compositions.

^f From VASE measurements [Och+18]. Similar fits were obtained by using data from [YH13] for AlInP.

Table A.5: Summary of semiconductor material parameters used for simulations of the main layers of GaAs solar cells.

Region	Materials			
	Ga _{0.51} In _{0.49} P Window	GaAs Emitter	GaAs Base	Al _{0.3} Ga _{0.7} As BSF
Band parameters ^a				
ϵ	11.8	12.8	12.8	12.2
E_g (eV)	1.85	1.42	1.42	1.73
N_C (cm ⁻³)	6.24·10 ¹⁷	4.21·10 ¹⁷	4.21·10 ¹⁷	6.07·10 ¹⁷
N_V (cm ⁻³)	1.46·10 ¹⁹	9.51·10 ¹⁸	9.51·10 ¹⁸	1.08·10 ¹⁹
n_i (cm ⁻³)	872	2.25·10 ⁶	2.25·10 ⁶	6970
Effective masses ^a				
m_n^*/m_0	0.088	0.067	0.067	0.083
m_p^*/m_0	0.695	0.48	0.48	0.6
Band offsets				
ΔE_V	0.15 · ΔE_g ^b		0.55 x^c	
$\Delta E_C : \Delta E_V$	13:87 ^d , 63:37 ^d			
Recombination Parameters ^a				
C_n (cm ⁶ /s)	4.7 · 10 ⁻³⁰	5 · 10 ⁻³⁰	5 · 10 ⁻³⁰	5 · 10 ⁻³⁰
C_p (cm ⁶ /s)	1.1 · 10 ⁻³⁰	10 ⁻³¹	10 ⁻³¹	10 ⁻³¹
B (cm ³ /s)	10 ⁻¹⁰	1.5 · 10 ⁻¹⁰ -2 · 10 ^{-10e}	1.5 · 10 ⁻¹⁰ -2 · 10 ^{-10e}	10 ⁻¹⁰
τ_p (ns)	4 · 10 ⁻³	See A.1.2	See A.1.2	1
τ_n (ns)	4 · 10 ⁻³	See A.1.2	See A.1.2	1
Optical constants				
n,k	In-house ^f	[Pal85]	[Pal85]	[Sil16]

^a From [LRS96] and [VMR01]. Due to the low content of indium (1.2%) in GaInAs for multijunction solar cells lattice matched to germanium, the material parameters are very similar to GaAs and they can be obtained from [LRS96]. The main difference is that of the bandgap which is ~ 1.4 eV.

^b From [Che+91]. See also [Gud+09b].

^c From [BW86].

^d From [Ada09].

^e From [Ste+13b] and data fitting.

^f From VASE measurements [Och+18].

Table A.6: Summary of semiconductor material parameters used for simulations of the main layers of Ge and GaNAsSb solar cells.

	Materials			
	Ga _{0.51} In _{0.49} P	Germanium	Germanium	GaNAsSb ^a
Region	Nucleation	Emitter	Base-Substrate	Absorber
Band parameters ^b				
ϵ	11.8	16	16	13
E_g (eV)	1.85	0.663	0.663	1.04 ^c
N_C (cm ⁻³)	6.24·10 ¹⁷	1.05·10 ¹⁹	1.05·10 ¹⁹	7.57·10 ¹⁷
N_V (cm ⁻³)	1.46·10 ¹⁹	3.95·10 ¹⁸	3.95·10 ¹⁸	9.48·10 ¹⁸
n_i (cm ⁻³)	872	1.73·10 ¹³	1.73·10 ¹³	4.92·10 ⁹
Effective masses				
m_n^*/m_0	0.088	0.56	0.56	0.097
m_p^*/m_0	0.695	0.29	0.29	0.52
Band offsets				
ΔE_V	See footnote ^d			$\sim 0.5 \cdot \Delta E_g$ ^e
Recombination Parameters ^b				
C_n (cm ⁶ /s)	4.7 · 10 ⁻³⁰	10 ^{-31f}	10 ^{-31f}	10 ⁻³¹
C_p (cm ⁶ /s)	1.1 · 10 ⁻³⁰	10 ^{-31f}	10 ^{-31f}	10 ⁻³¹
B (cm ³ /s)	10 ⁻¹⁰	6.41 · 10 ⁻¹⁴	6.41 · 10 ⁻¹⁴	2 · 10 ⁻¹⁰
τ_p (ns)	4 · 10 ⁻³	See A.1.3	See A.1.3	See A.2.2
τ_n (ns)	4 · 10 ⁻³	See A.1.3	See A.1.3	See A.2.2
Optical constants				
n,k	In-house ^g	[DN55]	[DN55]	In-house ^g

^a Band parameters are interpolations between ternary compounds GaNAs and GaNSb. Nominal composition is N=2.5% and Sb=6.5%.

^b From [LRS96] and [VMR01].

^c From QE. See section 5.3.2.

^d Applying Anderson's rule considering electron affinity of 4.01 and 4 eV for GaInP and Ge, respectively.

^e Heterojunction band offset between GaNAsSb/GaAs for a ~ 1 eV material. Data taken from [Yue06]. These values are highly dependent on the element composition of the alloy [Yue06].

^f From [GV06]. Different values may be found in [Sch05; VHG10].

^g From VASE measurements.

Bibliography

References

- [AD00] Carlos Algora and Vicente Díaz. “Influence of series resistance on guidelines for manufacture of concentrator p-on-n GaAs solar cells”. In: *Progress in Photovoltaics: Research and Applications* 8.2 (Mar. 2000), pp. 211–225. DOI: 10.1002/(SICI)1099-159X(200003/04)8:2<211::AID-PIP291>3.0.CO;2-D.
- [AD97] C. Algora and V. Díaz. “Performance and optimization of monochromatic heteroface Al-GaAs/GaAs photovoltaic cells”. In: *Solid-State Electronics* 41.11 (Nov. 1997), pp. 1787–1793. DOI: 10.1016/S0038-1101(97)00147-0.
- [Ada+13] Jessica G. J. Adams, Victor C. Elarde, Glen Hillier, Christopher Stender, Francis Tumminello, Andree Wibowo, Chris Youtsey, Zachary Bittner, Seth M. Hubbard, Eric B. Clark, Michael F. Piszczor, and Mark Osowski. “Improved radiation resistance of epitaxial lift-off inverted metamorphic solar cells”. In: *2013 IEEE 39th Photovoltaic Specialists Conference (PVSC)*. IEEE, June 2013, pp. 3229–3232. DOI: 10.1109/PVSC.2013.6745140.
- [Ada+94] Sadao Adachi, Hirokazu Kato, Akira Moki, and Kouji Ohtsuka. “Refractive index of $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ quaternary alloys”. In: *Journal of Applied Physics* 75.1 (1994), pp. 478–480. DOI: 10.1063/1.355824.
- [Ada09] S. Adachi. “Properties of Semiconductor Alloys : Group-IV , III - V and II - VI Semiconductors”. In: *John Wiley & Sons, Ltd.* 2009. Chap. 6, p. 391.

- [AKC09] H Arabshahi, M R Khalvati, and Monte Carlo. “Electronic Transport Studies of Bulk GaInP and AlGaInP Based on an Ensemble Monte Carlo Calculation Including Three-valley Band Structure Model”. In: (2009), pp. 61–64.
- [Alg+06] C. Algora, I. Rey-Stolle, B. Galiana, J. Gonzalez, M. Baudrit, and I. Garcia. “Strategic Options for a LED-Like Approach in III-V Concentrator Photovoltaics”. In: *2006 IEEE 4th World Conference on Photovoltaic Energy Conference*. Vol. 1. IEEE, 2006, pp. 741–744. DOI: 10.1109/WCPEC.2006.279562.
- [Alg07] C Algora. “Very-High-Concentration Challenges of III-V Multijunction Solar Cells”. In: *Concentrator Photovoltaics*. Ed. by Antonio L Luque and Andreev Viacheslav. Vol. 130. Springer Berlin Heidelberg, 2007, pp. 89–111.
- [Als+97] F. Alsina, M. Garriga, M. I. Alonso, S. Tortosa, J. Pascual, C. Geng, F. Scholz, and R. W. Glew. “Optical determination of growth variants in ordered GaInP”. In: *Solid State Communications* 101.10 (1997), pp. 757–760. DOI: 10.1016/S0038-1098(96)00652-7.
- [Alu04] M Alurralde. “Method using the primary knock-on atom spectrum to characterize electrical degradation of monocrystalline silicon solar cells by space protons”. In: *Journal of Applied Physics* 95.7 (2004), p. 3391.
- [Ari+17] Pieter Arickx, Rufi Kurstjens, Wim Geens, and Kristof Dessein. “The next generation of germanium substrates: EXPOGER.” In: *E3S Web of Conferences*. 16. 2017, p. 03010.
- [Asb77] P. Asbeck. “Self-absorption effects on the radiative lifetime in GaAs-GaAlAs double heterostructures”. In: *Journal of Applied Physics* 48.2 (1977), pp. 820–822. DOI: 10.1063/1.323633.
- [Atw11] Harry A. Atwater. “Paths to high efficiency low-cost photovoltaics”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference*. 2011, pp. 000001–000003. DOI: 10.1109/PVSC.2011.6185830.
- [BA07] M. Baudrit and C. Algora. “3D modeling of concentrator III-V multi-junction solar cells”. In: *Conference Record of the 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion, WCPEC-4 1* (2007), pp. 826–829. DOI: 10.1109/WCPEC.2006.279584.
- [BA08] M. Baudrit and C. Algora. “Modeling of GaInP/GaAs Dual-Junction Solar Cells including Tunnel Junction”. In: *33rd IEEE Photovoltaic Specialist Conference* (2008), pp. 1–5.
- [BA10] M. Baudrit and C. Algora. “Tunnel diode modeling, including nonlocal trap-assisted tunneling: A focus on III-V multijunction solar cell simulation”. In: *IEEE Transactions on Electron Devices* 57.10 (2010), pp. 2564–2571. DOI: 10.1109/TED.2010.2061771.

- [Bal04] José Lorenzo Manzanares Balenzategui. “Influencia del reciclaje de fotones en el funcionamiento y el diseño de células solares de arseniuro de galio.” Tesis Doctoral. Tesis Doctoral, Escuela Superior de Ingenieros Técnicos de Telecomunicación, Universidad Politécnica de Madrid, 2004.
- [Bar+09] E. Barrigón, I. Rey-Stolle, B. Galiana, I. García, and C. Algora. “GaInP/GaInAs/Ge triple junction solar cells for ultra high concentration”. In: *2009 Spanish Conference on Electron Devices* Mc (2009). DOI: 10.1109/SCED.2009.4800513.
- [Bar+13] E. Barrigón, S. Brückner, O. Supplie, H. Döscher, I. Rey-Stolle, and T. Hannappel. “In situ study of Ge(100) surfaces with tertiarybutylphosphine supply in vapor phase epitaxy ambient”. In: *Journal of Crystal Growth* 370 (May 2013), pp. 173–176. DOI: 10.1016/j.jcrysgro.2012.07.046.
- [Bar+14] Enrique Barrigón, Ivan García, Laura Barrutia, Ignacio Rey-Stolle, and Carlos Algora. “Highly conductive p++-AlGaAs/n++-GaInP tunnel junctions for ultra-high concentrator solar cells”. In: *Progress in Photovoltaics: Research and Applications* 22.4 (Apr. 2014), pp. 399–404. DOI: 10.1002/pip.2476.
- [Bar+15a] E. Barrigón, P. Espinet-González, Y. Contreras, and I. Rey-Stolle. “Implications of low breakdown voltage of component subcells on external quantum efficiency measurements of multijunction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 23.11 (Nov. 2015), pp. 1597–1607. DOI: 10.1002/pip.2597.
- [Bar+15b] L. Barrutia, E. Barrigón, L. Lopez-Conesa, J. Rebled, S. Estrade, F. Peiro, I. Rey-Stolle, and C. Algora. “On the use of Sb to improve the performance of GaInP subcells of multijunction solar cells”. In: *2015 IEEE 42nd Photovoltaic Specialist Conference, PVSC 2015* (2015). DOI: 10.1109/PVSC.2015.7356354.
- [Bar+16] E. Barrigón, L. Barrutia, M. Ochoa, I. Rey-Stolle, and Carlos Algora. “Effect of Sb on the quantum efficiency of GaInP solar cells”. In: *Prog. Photovolt: Res. Appl.* 24 (2016), pp. 1116–1122. DOI: 10.1002/pip.2777.
- [Bar+17] Laura Barrutia, Enrique Barrigón, Iván García, Ignacio Rey-Stolle, and Carlos Algora. “Effect of Ge autodoping during III-V MOVPE growth on Ge substrates”. In: *Journal of Crystal Growth* (2017). DOI: 10.1016/j.jcrysgro.2017.06.022.
- [Bar+18] Enrique Barrigón, Mario Ochoa, Ivan García, Laura Barrutia, Carlos Algora, and Ignacio Rey-Stolle. “Degradation of Ge subcells by thermal load during the growth of multijunction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 26.2 (2018), pp. 102–111. DOI: 10.1002/pip.2948.
- [Bar14] Enrique Barrigón. “Development of GaInP/GaInAs/Ge triple-junction solar cells for CPV applications”. PhD thesis. IES-UPM, 2014.

- [Bar17] Laura Barrutia. “Optimization pathways to improve GaInP/GaInAs/Ge triple junction solar cells for CPV applications”. PhD thesis. IES-UPM, 2017.
- [Bar87] Allen M. Barnett. “The Spectral p-n Junction Model for Tandem Solar-Cell Design”. In: *IEEE Transactions on Electron Devices* 34.2 (1987), pp. 257–266. DOI: 10.1109/T-ED.1987.22916.
- [Bau+07] Carsten Baur, Martin Hermle, Frank Dimroth, and Andreas W. Bett. “Effects of optical coupling in III-V multilayer systems”. In: *Applied Physics Letters* 90.19 (2007), pp. 1–4. DOI: 10.1063/1.2737927.
- [Bau+16] Gerard Bauhuis, Peter Mulder, Yu-Ying Hu, and John Schermer. “Deep junction III-V solar cells with enhanced performance”. In: *physica status solidi (a)* 213.8 (Aug. 2016), pp. 2216–2222. DOI: 10.1002/pssa.201532903.
- [Ben+10a] N. Ben Sedrine, C. Bouhafs, J. C. Harmand, R. Chtourou, and V. Darakchieva. “Effect of nitrogen on the GaAs_{0.9}-xNxSb_{0.1} dielectric function from the near-infrared to the ultraviolet”. In: *Applied Physics Letters* 97.20 (2010), p. 201903. DOI: 10.1063/1.3518479.
- [Ben+10b] Pablo Benítez, Juan C Miñano, Pablo Zamora, Rubén Mohedano, Aleksandra Cvetkovic, Marina Buljan, Julio Chaves, and Maikel Hernández. “High performance Fresnel-based photovoltaic concentrator.” In: *Optics express* 18.9 (2010), A25–A40. DOI: 10.1364/OE.18.000A25.
- [BK06] Abderrahmane Belghachi and Samira Khelifi. “Modelling of the perimeter recombination effect in GaAs-based micro-solar cell”. In: *Solar Energy Materials and Solar Cells* 90.1 (2006), pp. 1–14. DOI: 10.1016/j.solmat.2005.01.009.
- [Bla62] J.S. Blakemore. “Semiconductor Statistics”. In: *Semiconductor Statistics*. 1962, pp. 343–345. DOI: 10.1016/B978-0-08-009592-9.50015-7. arXiv: arXiv:1011.1669v3.
- [Bla82] J. S. Blakemore. “Semiconducting and other major properties of gallium arsenide”. In: *Journal of Applied Physics* 53.10 (1982). DOI: 10.1063/1.331665. arXiv: arXiv:1011.1669v3.
- [Bou90] J C Bourgoin. *Physics of DX Centers in GaAs Alloys*. Diffusion and defect data, solid state data: Solid state phenomena. Sci-Tech Publications, 1990.
- [Bou93] David P. Bour. “Chapter 9 - AlGaInP Quantum Well Lasers”. In: *Quantum Well Lasers*. 1993, pp. 415–460. DOI: 10.1016/B978-0-08-051558-8.50015-4.

- [Bra+11] Avi Braun, Nadine Szabó, Klaus Schwarzburg, Thomas Hannappel, Eugene a. Katz, and Jeffrey M. Gordon. “Current-limiting behavior in multijunction solar cells”. In: *Applied Physics Letters* 98.22 (2011), pp. 3–5. DOI: 10.1063/1.3596444.
- [Bro+15] Lirong Z. Broderick, Brian R. Albert, Brian S. Pearson, Lionel C. Kimerling, and Jurgen Michel. “Design for energy: Modeling of spectrum, temperature and device structure dependences of solar cell energy production”. In: *Solar Energy Materials and Solar Cells* 136 (2015), pp. 48–63. DOI: 10.1016/j.solmat.2014.12.034.
- [Bro+17] C. R. Brown, N. J. Estes, V. R. Whiteside, B. Wang, K. Hossain, T. D. Golding, M. Leroux, M Al Khalfioui, J. G. Tischler, C. T. Ellis, E. R. Glaser, and I. R. Sellers. “The effect and nature of N-H complexes in the control of the dominant photoluminescence transitions in UV-hydrogenated GaInNAs”. In: *RSC Advances* 7.41 (May 2017), pp. 25353–25361. DOI: 10.1039/c7ra02900d.
- [Bue+15] J. Buencuerpo, J. M. Llorens, M. L. Dotor, and J. M. Ripalda. “Broadband antireflective nano-cones for tandem solar cells”. In: *Optics Express* 23.7 (Apr. 2015), A322. DOI: 10.1364/OE.23.00A322.
- [BW86] J. Batey and S. L. Wright. “Energy band alignment in GaAs:(Al,Ga)As heterostructures: The dependence on alloy composition”. In: *Journal of Applied Physics* 59.1 (Jan. 1986), p. 200. DOI: 10.1063/1.336864.
- [BW94] Max Born and Emil Wolf. *Principles of optics: Electromagnetic Theory of Propagation, Interference and Diffraction of Light*. Pergamon Press, 1994, pp. 1–952. DOI: 10.1016/S0030-3992(00)00061-X. arXiv: arXiv:1011.1669v3.
- [CB14] A. Chroneos and H. Bracht. “Diffusion of n -type dopants in germanium”. In: *Applied Physics Reviews* 1.1 (2014). DOI: 10.1063/1.4838215.
- [CB97b] Donald A Clugston and Paul A Basore. “Modelling Free-carrier Absorption in Solar Cells”. In: *Progress in Photovoltaics Research and Applications* 5.4 (1997), pp. 229–236. DOI: 10.1002/(SICI)1099-159X(199707/08)5:4<229::AID-PIP164>3.3.CO;2-Y.
- [Cen05] Emanuele Centurioni. “Generalized matrix method for calculation of internal light energy flux in mixed coherent and incoherent multilayers.” In: *Applied optics* 44.35 (2005), pp. 7532–7539. DOI: 10.1364/AO.44.007532.
- [Che+91] Jianhui Chen, J. R. Sites, I. L. Spain, M. J. Hafich, and G. Y. Robinson. “Band offset of GaAs/In_{0.48}Ga_{0.52}P measured under hydrostatic pressure”. In: *Applied Physics Letters* 58.7 (Feb. 1991), pp. 744–746. DOI: 10.1063/1.104534.

- [Cia+89] P Ciampolini, A Pierantoni, M Melanotte, C Cecchetti, C Lombardi, and G Baccarani. “Realistic device simulation in three dimensions [{EPROM} cell]”. In: *Electron Devices Meeting, 1989. IEDM '89. Technical Digest., International*. 1989, pp. 131–134. DOI: 10.1109/IEDM.1989.74244.
- [Coi+11] J. Coignus, M. Baudrit, J. Singer, R. Lachaume, D. Muñoz, and P. Thony. “Key issues for accurate simulation of a-Si:H / c-Si heterojunction solar cells”. In: *Energy Procedia* 8.2010 (2011), pp. 174–179. DOI: 10.1016/j.egypro.2011.06.120.
- [Col09] E. A.B. Cole. *Mathematical and numerical modelling of heterostructure semiconductor devices: From theory to programming*. 2009, pp. 1–406. DOI: 10.1007/978-1-84882-937-4.
- [CT67] D M Caughey and R E Thomas. “Carrier mobilities in silicon empirically related to doping and field”. In: *Proceedings of the IEEE* 55.12 (1967), pp. 2192–2193.
- [DA01] V Díaz and C Algora. “Effects of the size and shape of GaAs solar cells on recombination losses”. In: *Actas 3ra. Conferencia Dispositivos Electr{ó}nicos*. 2001.
- [Dag+16] R Dagan, Y Rosenwaks, A Kribus, A W Walker, J Ohlmann, and F Dimroth. “Minority carrier recombination of ordered Ga_{0.51}In_{0.49}P at high temperatures”. In: *Applied Physics Letters* 109.22 (2016), pp. 0–4. DOI: 10.1063/1.4971282.
- [Dai+15] P. Dai, M. Tan, Y.Y. Wu, L. Ji, L.F. Bian, S.L. Lu, and H. Yang. “Solid-state tellurium doping of AlInP and its application to photovoltaic devices grown by molecular beam epitaxy”. In: *Journal of Crystal Growth* 413 (2015), pp. 71–75. DOI: 10.1016/j.jcrysgro.2014.12.014.
- [DeL+95] M. C. DeLong, D. J. Mowbray, R. a. Hogg, M. S. Skolnick, J. E. Williams, K. Meehan, Sarah R. Kurtz, J. M. Olson, R. P. Schneider, M. C. Wu, and M. Hopkinson. “Band gap of “completely disordered” Ga_{0.52}In_{0.48}P”. In: *Applied Physics Letters* 66.23 (1995), p. 3185. DOI: 10.1063/1.113717.
- [Dim+14] Frank Dimroth et al. “Wafer bonded four-junction GaInP/GaAs//GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency”. In: *Progress in Photovoltaics: Research and Applications* 22.3 (Mar. 2014), pp. 277–282. DOI: 10.1002/pip.2475.
- [Dim+16] Frank Dimroth et al. “Four-junction wafer-bonded concentrator solar cells”. In: *IEEE Journal of Photovoltaics* 6.1 (Jan. 2016), pp. 343–349. DOI: 10.1109/JPHOTOV.2015.2501729.
- [DN55] W. C. Dash and R. Newman. “Intrinsic Optical Absorption in Single-Crystal Germanium and Silicon at 77°K and 300°K”. In: *Physical Review* 99.4 (Aug. 1955), pp. 1151–1155. DOI: 10.1103/PhysRev.99.1151.

- [Dod+91] Paul E. Dodd, Theresa B. Stellwag, Michael R. Melloch, and Mark S. Lundstrom. “Surface and perimeter recombination in GaAs diodes: An experimental and theoretical investigation”. In: *IEEE Transactions on Electron Devices* 38.6 (1991), pp. 1253–1261. DOI: 10.1109/16.81614.
- [Dod93] P E Dodd. “Studies of Heterojunction Bipolar Transistor Device Physics and New Device Concepts”. PhD thesis. 1993.
- [Dum57] William P. Dumke. “Spontaneous radiative recombination in semiconductors”. In: *Physical Review* 105.1 (1957), pp. 139–144. DOI: 10.1103/PhysRev.105.139.
- [Dun54] W. C. Dunlap. “Diffusion of Impurities in Germanium”. In: *Physical Review* 94.6 (June 1954), pp. 1531–1540. DOI: 10.1103/PhysRev.94.1531.
- [Dut00] Robert W. Dutton. “Perspectives on technology and technology-driven CAD”. In: *IEEE Transactions on Computer-Aided Design of Integrated Circuits and Systems* 19.12 (2000), pp. 1544–1560. DOI: 10.1109/43.898831.
- [Eme11] Keith Emery. “Measurement and characterization of solar cells and modules”. In: *Handbook of Photovoltaic Science and Engineering*. 2nd. W. Sussex, UK: John Wiley & Sons, 2011. Chap. 18, pp. 797–840. DOI: 10.1002/0470014008.ch16.
- [Erk10] Katrin. Erk. *Dilute III-V nitride semiconductors and material systems : physics and technology*. Springer, 2010.
- [Ero08] Ayse. Erol. *Dilute III-V nitride semiconductors and material systems : physics and technology*. Springer, 2008, p. 590.
- [Esp+10] P Espinet, C Algora, J R González, Neftalí Núñez, and M Vázquez. “Degradation mechanism analysis in temperature stress tests on III-V ultra-high concentrator solar cells using a 3D distributed model”. In: *Microelectronics Reliability* 50.9-11 (2010), pp. 1875–1879. DOI: 10.1016/j.microrel.2010.07.128.
- [Esp+15a] P. Espinet-González, C. Algora, N. Núñez, V. Orlando, M. Vázquez, J. Bautista, and K. Araki. “Temperature accelerated life test on commercial concentrator III-V triple-junction solar cells and reliability analysis as a function of the operating temperature”. In: *Progress in Photovoltaics: Research and Applications* 23.5 (May 2015), pp. 559–569. DOI: 10.1002/pip.2461.
- [Esp+15b] P Espinet-González, I Rey-Stolle, M Ochoa, C Algora, I García, and E Barrigón. “Analysis of perimeter recombination in the subcells of GaInP/GaAs/Ge triple-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 23.7 (2015), pp. 874–882. DOI: 10.1002/pip.2501.

- [Ess+15] Stephanie Essig, Scott Ward, Myles A. Steiner, Daniel J. Friedman, John F. Geisz, Paul Stradins, and David L. Young. “Progress Towards a 30% Efficient GaInP/Si Tandem Solar Cell”. In: *Energy Procedia* 77 (Aug. 2015), pp. 464–469. DOI: 10.1016/j.egypro.2015.07.066.
- [Ess+16] Stephanie Essig et al. “Realization of GaInP/Si Dual-Junction Solar Cells With 29.8% 1-Sun Efficiency”. In: *IEEE Journal of Photovoltaics* 6.4 (July 2016), pp. 1012–1019. DOI: 10.1109/JPHOTOV.2016.2549746.
- [Fer+02] R. Ferrini, G. Guizzetti, M. Patrini, A. Parisini, L. Tarricone, and B. Valenti. “Optical functions of InGaP/GaAs epitaxial layers from 0.01 to 5.5 eV”. In: *European Physical Journal B* 27.4 (2002), pp. 449–458. DOI: 10.1140/epjb/e2002-00177-x.
- [Fer+07] J Fernández, F Dimroth, E Oliva, M Hermle, and A W Bett. “Back-surface Optimization of Germanium TPV Cells”. In: *AIP Conference Proceedings An Overview of TPV Cell Technologies AIP Conference Proceedings AIP Conference Proceedings Journal of Applied Physics* 8901.10 (2007). DOI: 10.1063/1.1539384.
- [Fer+08] Jara Fernandez, Stefan Janz, Dominik Suwito, Eduard Oliva, and Frank Dimroth. “Advanced concepts for high-efficiency germanium photovoltaic cells”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference*. IEEE, May 2008, pp. 1–4. DOI: 10.1109/PVSC.2008.4922631.
- [Fet+02] C. M. Fetzer, R. T. Lee, G. B. Stringfellow, X. Q. Liu, a. Sasaki, and N. Ohno. “Effect of surfactant Sb on carrier lifetime in GaInP epilayers”. In: *Journal of Applied Physics* 91.1 (2002), pp. 199–203. DOI: 10.1063/1.1423396.
- [FF10] Stephen J. Fonash and Stephen J. Fonash. “Chapter Four - Homojunction Solar Cells”. In: *Solar Cell Device Physics*. 2010, pp. 121–182. DOI: 10.1016/B978-0-12-374774-7.00004-2.
- [FGS13] Daniel J. Friedman, John F. Geisz, and Myles a. Steiner. “Analysis of Multijunction Solar Cell Current-Voltage Characteristics in the Presence of Luminescent Coupling”. In: *IEEE Journal of Photovoltaics* 3.4 (2013), pp. 1429–1436. DOI: 10.1109/JPHOTOV.2013.2275189.
- [FGS14] Daniel J. Friedman, John F. Geisz, and Myles A. Steiner. “Effect of Luminescent Coupling on the Optimal Design of Multijunction Solar Cells”. In: *IEEE Journal of Photovoltaics* 4.3 (May 2014), pp. 986–990. DOI: 10.1109/JPHOTOV.2014.2308722.
- [Fid+14] Onur Fidaner, Ferran a. Suarez, Michael Wiemer, Vijit a. Sabnis, Tetsuya Asano, Akihiro Itou, Daijiro Inoue, Nobuhiko Hayashi, Hidekazu Arase, Akio Matsushita, and Tohru Nakagawa. “High efficiency micro solar cells integrated with lens array”. In: *Applied Physics Letters* 104.10 (2014). DOI: 10.1063/1.4868116.

- [FO01] D. J. Friedman and J. M. Olson. “Analysis of Ge junctions for GaInP/GaAs/Ge three-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 9.3 (2001), pp. 179–189. DOI: 10.1002/pip.365.
- [Fon10] Stephen J. Fonash. “Material Properties and Device Physics Basic to Photovoltaics”. In: *Solar Cell Device Physics*. Academic Press/Elsevier, 2010, pp. 9–65. DOI: 10.1016/B978-0-12-374774-7.00002-9. arXiv: arXiv:1011.1669v3.
- [Fos76b] Jerry G. Fossum. “Computer-aided numerical analysis of silicon solar cells”. In: *Solid State Electronics* 19.4 (Apr. 1976), pp. 269–277. DOI: 10.1016/0038-1101(76)90022-8.
- [Fra+15] Ryan M. France, John F. Geisz, Ivan Garcia, Myles A. Steiner, William E. McMahon, Daniel J. Friedman, Tom E. Moriarty, Carl Osterwald, J. Scott Ward, Anna Duda, Michelle Young, and Waldo J. Olavarria. “Quadruple-Junction Inverted Metamorphic Concentrator Devices”. In: *IEEE Journal of Photovoltaics* 5.1 (Jan. 2015), pp. 432–437. DOI: 10.1109/JPHOTOV.2014.2364132.
- [Fri+05] D.J. Friedman, a.J. Ptak, S.R. Kurtz, and J.F. Geisz. “Analysis of depletion-region collection in GaInNAs solar cells”. In: *Conference Record of the Thirty-first IEEE Photovoltaic Specialists Conference, 2005*. February (2005), pp. 4–7. DOI: 10.1109/PVSC.2005.1488225.
- [Fri+13] Daniel J. Friedman, Richard R. King, Richard M. Swanson, Jennifer McJannet, and Don Gwinner. *Editorial: Toward 100 gigawatts of concentrator photovoltaics by 2030*. Oct. 2013. DOI: 10.1109/JPHOTOV.2013.2270341.
- [Fri+98] D J Friedman, J F Geisz, S R Kurtz, and J M Olson. “1-eV solar cells with GaInNAs active layer”. In: *Journal of Crystal Growth* 195.1 (1998), pp. 409–415. DOI: 10.1016/S0022-0248(98)00561-2.
- [Gal+05] Beatriz Galiana, Carlos Algora, I. Rey-Stolle, and I. Vara. “A 3-D Model for Concentrator Solar Cells Based on Distributed Circuit Units”. In: *IEEE Transactions on Electron Devices* 52.12 (2005), pp. 2552–2558. DOI: 10.1109/TED.2005.859620.
- [Gal+06] Beatriz Galiana, Ignacio Rey-Stolle, Mathieu Baudrit, Iván García, and Carlos Algora. “A comparative study of BSF layers for GaAs-based single-junction or multijunction concentrator solar cells”. In: *Semiconductor Science and Technology* 21.10 (2006), pp. 1387–1392. DOI: 10.1088/0268-1242/21/10/003.
- [Gar+09] I. García, I. Rey-Stolle, B. Galiana, and C. Algora. “A 32.6% efficient lattice-matched dual-junction solar cell working at 1000 suns”. In: *Applied Physics Letters* 94.5 (2009), pp. 5–8. DOI: 10.1063/1.3078817.

- [Gar+17b] Ivan García, Mario Ochoa, Iván Lombardero, Luis Cifuentes, Manuel Hinojosa, Pablo Caño, Ignacio Rey-Stolle, Carlos Algora, Andrew Johnson, Iwan Davies, Kian Hua Tan, Wan Khai Loke, Satrio Wicaksono, and Soon Fatt Yoon. “Degradation of subcells and tunnel junctions during growth of GaInP/Ga(In)As/GaNAsSb/Ge 4-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 25.11 (Sept. 2017), pp. 887–895. DOI: 10.1002/pip.2930.
- [GAR06] Beatriz Galiana, Carlos Algora, and Ignacio Rey-Stolle. “Comparison of 1D and 3D analysis of the front contact influence on GaAs concentrator solar cell performance”. In: *Solar Energy Materials and Solar Cells* 90.16 (2006), pp. 2589–2604. DOI: 10.1016/j.solmat.2006.02.013.
- [Gar10] Iván García. “Desarrollo de células solares de doble unión GaInP/GaAs para concentraciones luminosas elevadas”. PhD thesis. IES-UPM, 2010.
- [Gau+07] E. Gaubas, J. Vanhellemont, E. Simoen, I. Romandic, W. Geens, and P. Clauws. “Carrier lifetime dependence on doping, metal implants and excitation density in Ge and Si”. In: *Physica B: Condensed Matter* 401-402 (2007), pp. 222–225. DOI: 10.1016/j.physb.2007.08.151.
- [Gei+07] J. F. Geisz, Sarah Kurtz, M. W. Wanlass, J. S. Ward, A. Duda, D. J. Friedman, J. M. Olson, W. E. McMahon, T. E. Moriarty, and J. T. Kiehl. “High-efficiency GaInP/GaAs/InGaAs triple-junction solar cells grown inverted with a metamorphic bottom junction”. In: *Applied Physics Letters* 91.2 (July 2007), p. 023502. DOI: 10.1063/1.2753729.
- [Gei+13] J. F. Geisz, M. a. Steiner, I. García, S. R. Kurtz, and D. J. Friedman. “Enhanced external radiative efficiency for 20.8% efficient single-junction GaInP solar cells”. In: *Applied Physics Letters* 103.4 (2013). DOI: 10.1063/1.4816837.
- [Gei+14] John F. Geisz, Ryan M. France, Iván García, Myles A. Steiner, and Daniel J. Friedman. “Device characterization for design optimization of 4 junction inverted metamorphic concentrator solar cells”. In: *AIP Conference Proceedings*. Vol. 1616. 2014, pp. 114–118. DOI: 10.1063/1.4897041.
- [Gei+15a] John F. Geisz, Iván García, William E. McMahon, Myles A. Steiner, Mario Ochoa, Ryan M. France, Aron Habte, and Daniel J. Friedman. “Energy yield determination of concentrator solar cells using laboratory measurements”. In: *11th International Conference on Concentrator Photovoltaic Systems: CPV-11*. Vol. 1679. AIP Publishing, Sept. 2015, p. 040005. DOI: 10.1063/1.4931516.

- [Gei+15b] John F. Geisz, Myles A. Steiner, Ivan Garcia, Ryan M. France, William E. McMahon, Carl R. Osterwald, and Daniel J. Friedman. “Generalized Optoelectronic Model of Series-Connected Multijunction Solar Cells”. In: *IEEE Journal of Photovoltaics* 5.6 (2015), pp. 1–13. DOI: 10.1109/JPHOTOV.2015.2478072.
- [Gei+98] J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz, and B.M. Keyes. “Photocurrent of 1eV GaInNAs lattice-matched to GaAs”. In: *Journal of Crystal Growth* 195.1-4 (1998), pp. 401–408. DOI: 10.1016/S0022-0248(98)00563-6.
- [GF02] J F Geisz and D J Friedman. “III-N-V semiconductors for solar photovoltaic applications”. In: *Semiconductor Science and Technology* 17.8 (2002), pp. 769–777. DOI: 10.1088/0268-1242/17/8/305.
- [Gho+14] Kanchan Ghosal, Doug Lilly, John Gabriel, and Scott Burroughs. “Semprius field results”. In: *AIP Conference Proceedings*. Vol. 1616. 2014, pp. 272–275. DOI: 10.1063/1.4897076.
- [GOY90] N Goto, Y Ohno, and H Yano. “Two-dimensional numerical simulation of side-gating effect in GaAs MESFETs”. In: *Electron Devices, IEEE Transactions on* 37.8 (1990), pp. 1821–1827.
- [GRA12a] I García, I Rey-Stolle, and C Algora. “Performance analysis of AlGaAs/GaAs tunnel junctions for ultra-high concentration photovoltaics”. In: *Journal of Physics D: Applied Physics* 45.4 (2012), p. 045101. DOI: 10.1088/0022-3727/45/4/045101.
- [GRA12b] I García, I Rey-Stolle, and C Algora. “Performance analysis of AlGaAs/GaAs tunnel junctions for ultra-high concentration photovoltaics”. In: *Journal of Physics D: Applied Physics* 45.4 (2012), p. 045101. DOI: 10.1088/0022-3727/45/4/045101.
- [Gre12] Martin A. Green. “Radiative efficiency of state-of-the-art photovoltaic cells”. In: *Progress in Photovoltaics: Research and Applications* 20.4 (June 2012), pp. 472–476. DOI: 10.1002/pip.1147.
- [Gub+14] Alexander Gubanov, Ville Polojärvi, Arto Aho, Antti Tukiainen, Nikolai V Tkachenko, and Mircea Guina. “Dynamics of time-resolved photoluminescence in GaInNAs and GaNAsSb solar cells.” In: *Nanoscale research letters* 9.1 (Jan. 2014), p. 80. DOI: 10.1186/1556-276X-9-80.
- [Gud+08] A. S. Gudovskikh, N. A. Kaluzhniy, V. M. Lantratov, S. A. Mintairov, M. Z. Shvarts, and V. M. Andreev. “Numerical modelling of GaInP solar cells with AlInP and AlGaAs windows”. In: *Thin Solid Films* 516.20 (2008), pp. 6739–6743. DOI: 10.1016/j.tsf.2007.12.016.

- [Gud+09a] A S Gudovskikh, J P Kleider, R Chouffot, N a Kalyuzhnyy, S a Mintairov, and V M Lantratov. “III-phosphides heterojunction solar cell interface properties from admittance spectroscopy”. In: *Journal of Physics D: Applied Physics* 42.16 (2009), p. 165307. DOI: 10.1088/0022-3727/42/16/165307.
- [Gud+09b] A S Gudovskikh, J P Kleider, R Chouffot, N a Kalyuzhnyy, S a Mintairov, and V M Lantratov. “III-phosphides heterojunction solar cell interface properties from admittance spectroscopy”. In: *Journal of Physics D: Applied Physics* 42.16 (2009), p. 165307. DOI: 10.1088/0022-3727/42/16/165307.
- [Gud+12] A. S. Gudovskikh, K. S. Zelentsov, N. A. Kalyuzhnyy, V. V. Evstropov, V. M. Lantratov, and S. A. Mintairov. “Interface properties of GaInP/Ge hetero-structure sub-cells of multi-junction solar cells”. In: *Journal of Physics D: Applied Physics* 45.49 (2012), p. 495305. DOI: 10.1088/0022-3727/45/49/495305.
- [Gum64] H. K. Gummel. “A Self-Consistent Iterative Scheme for One-Dimensional Steady State Transistor Calculations”. In: *IEEE Transactions on Electron Devices* 11.10 (Oct. 1964), pp. 455–465. DOI: 10.1109/T-ED.1964.15364.
- [GV06] E. Gaubas and J. Vanhellemont. “Dependence of carrier lifetime in germanium on resistivity and carrier injection level”. In: *Applied Physics Letters* 89.14 (2006), pp. 23–26. DOI: 10.1063/1.2358967.
- [GVA16a] Iván García, Marta Victoria, and Ignacio Antón. “Temperature Effects on CPV Solar Cells, Optics and Modules”. In: *Handbook on Concentrator Photovoltaic Technology*. Chichester, West Sussex: John Wiley & Sons, Ltd, Apr. 2016, pp. 246–290. DOI: 10.1002/9781118755655.ch05.
- [GVA16b] Iván García, Marta Victoria, and Ignacio Antón. “Temperature Effects on CPV Solar Cells, Optics and Modules”. In: *Handbook of Concentrator Photovoltaic Technology*. Chichester, West Sussex: John Wiley & Sons, Ltd, Apr. 2016, pp. 245–292. DOI: 10.1002/9781118755655.ch05.
- [Haa+11] Alexander W. Haas, John R. Wilcox, Jeffery L. Gray, and Richard J. Schwartz. “Design of a GaInP/GaAs tandem solar cell for maximum daily, monthly, and yearly energy output”. In: *Journal of Photonics for Energy* 1.1 (2011), p. 018001. DOI: 10.1117/1.3633244.
- [Hae+09] N. M. Haegel, T. J. Mills, M. Talmadge, C. Scandrett, C. L. Frenzen, H. Yoon, C. M. Fetzer, and R. R. King. “Direct imaging of anisotropic minority-carrier diffusion in ordered GaInP”. In: *Journal of Applied Physics* 105.2 (2009), pp. 1–6. DOI: 10.1063/1.3068196.

- [Hae+14] N. M. Haegel, T. Christian, C. Scandrett, A. G. Norman, A. Mascarenhas, Pranob Misra, Ting Liu, Arsen Sukiasyan, Evan Pickett, and Homan Yuen. “Doping dependence and anisotropy of minority electron mobility in molecular beam epitaxy-grown p type GaInP”. In: *Applied Physics Letters* 105.20 (Nov. 2014), p. 202116. DOI: 10.1063/1.4902316.
- [Har+02] J-C Harmand, A Caliman, E V K Rao, L Largeau, J Ramos, R Teissier, L Travers, G Ungaro, B Theys, and I F L Dias. “GaNASb: how does it compare with other dilute III V-nitride alloys?” en. In: *Semiconductor Science and Technology* 17.8 (Aug. 2002), pp. 778–784. DOI: 10.1088/0268-1242/17/8/306.
- [Har+05] J.S. Harris, H. Yuen, S. Bank, M. Wistey, V. Lordi, T. Gugov, H. Bae, and L. Goddard. “MBE Growth and Characterization of Long Wavelength Dilute Nitride III-V Alloys”. In: *Dilute Nitride Semiconductors*. 2005. Chap. 1, pp. 1–92. DOI: 10.1016/B978-008044502-1/50001-9.
- [Har+07] James S. Harris, R. Kudrawiec, H. B. Yuen, S. R. Bank, H. P. Bae, M. a. Wistey, D. Jackrel, E. R. Pickett, T. Sarmiento, L. L. Goddard, V. Lordi, and T. Gugov. “Development of GaInNASb alloys: Growth, band structure, optical properties and applications”. In: *Physica Status Solidi (B) Basic Research* 244.8 (2007), pp. 2707–2729. DOI: 10.1002/pssb.200675620.
- [Hay55] J. R. Haynes. “New Radiation Resulting from Recombination of Holes and Electrons in Germanium”. In: *Physical Review* 98.6 (June 1955), pp. 1866–1868. DOI: 10.1103/PhysRev.98.1866.
- [HB12] R. Hoheisel and a. W. Bett. “Experimental analysis of majority carrier transport processes at heterointerfaces in photovoltaic devices”. In: *IEEE Journal of Photovoltaics* 2.3 (2012), pp. 398–402. DOI: 10.1109/JPHOTOV.2012.2199080.
- [Hec+13] Stefan Heckelmann, David Lackner, Frank Dimroth, and Andreas W. Bett. “Al_xGa_{1-x}As minority carrier lifetime enhancement at low temperatures”. In: *Applied Physics Letters* 103.13 (2013), pp. 1–4. DOI: 10.1063/1.4822432.
- [Hen05] Mohamed. Henini. *Dilute nitride semiconductors*. Elsevier, 2005, p. 630.
- [Her+08] Martin Hermle, Simon P Philipps, Gergo Letay, and Andreas W Bett. “Numerical Simulation of Tunnel Diodes and Multi-Junction Solar Cells”. In: *33rd IEEE Photovoltaic Specialist Conference* (2008), pp. 10–13. DOI: 10.1109/PVSC.2008.4922544.
- [Her+12] Rebeca Herrero, Marta Victoria, César Domínguez, Stephen Askins, Ignacio Antón, and Gabriel Sala. “Concentration photovoltaic optical system irradiance distribution measurements and its effect on multi-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 20.4 (June 2012), pp. 423–430. DOI: 10.1002/pip.1145.

- [HHF00] Yue Ming Hsin, Shih Tzung Hsu, and Chen Chung Fan. “Electron saturation velocity of GaInP deduced in a GaInP/GaAs/GaInP double heterojunction bipolar transistor”. In: *Applied Physics Letters* 77.10 (2000), pp. 1538–1539. DOI: 10.1063/1.1290602.
- [Hil74] C. Hilsum. “Simple empirical relationship between mobility and carrier concentration”. In: *Electronics Letters* 10.13 (1974), pp. 259–260.
- [HKK92] G. A.M. Hurkx, D. B.M. Klaassen, and M. P.G. Knuvers. “A New Recombination Model for Device Simulation Including Tunneling”. In: *IEEE Transactions on Electron Devices* 39.2 (1992), pp. 331–338. DOI: 10.1109/16.121690.
- [HLM78] C H Henry, R A Logan, and F R Merritt. “The effect of surface recombination on current in $\{Al_xGa_{1-x}As\}$ heterojunctions”. In: *Journal of Applied Physics* 49.6 (1978), pp. 3530–3542. DOI: 10.1063/1.325265.
- [Hoh+10] Raymond Hoheisel, Jara Fernandez, Frank Dimroth, and Andreas W Bett. “Investigation of radiation hardness of germanium photovoltaic cells”. In: *IEEE Transactions on Electron Devices* 57.9 (2010), pp. 2190–2194. DOI: 10.1109/TED.2010.2053491.
- [Hoh+13] Raymond Hoheisel, Frank Dimroth, Andreas W. Bett, Scott R. Messenger, Phillip P. Jenkins, and Robert J. Walters. “Electroluminescence analysis of irradiated GaInP/GaInAs/Ge space solar cells”. In: *Solar Energy Materials and Solar Cells* 108 (2013), pp. 235–240. DOI: 10.1016/j.solmat.2012.06.015.
- [Hov75] H J Hovel. *Semiconductors and semimetals. Volume 11. Solar cells*. Academic Press, Inc., New York, 1975.
- [Hwa+16] Sun-Tae Hwang, Soohyun Kim, Hyeunseok Cheun, Hyun Lee, Byungho Lee, Taehyun Hwang, Sangheon Lee, Wonki Yoon, Heon-Min Lee, and Byungwoo Park. “Bandgap grading and $Al_{0.3}Ga_{0.7}As$ heterojunction emitter for highly efficient GaAs-based solar cells”. In: *Solar Energy Materials and Solar Cells* 155 (2016), pp. 264–272. DOI: 10.1016/j.solmat.2016.06.009.
- [HY90] Kazushige Horio and Hisayoshi Yanai. “Numerical modeling of heterojunctions including the thermionic emission mechanism at the heterojunction interface”. In: *IEEE Transactions on Electron Devices* 37.4 (1990), pp. 1093–1098. DOI: 10.1109/16.52447.
- [IK89] M. Ikeda and K. Kaneko. “Selenium and zinc doping in $Ga_{0.5}In_{0.5}P$ and $(Al_{0.5}Ga_{0.5})_{0.5}In_{0.5}P$ grown by metalorganic chemical vapor deposition”. In: *Journal of Applied Physics* 66.11 (Dec. 1989), pp. 5285–5289. DOI: 10.1063/1.343718.

- [Ima+02] M. Imaizumi, T. Takamoto, T. Ohshima, M. Yamaguchi, H. Itoh, and Matsuda S. “Radiation effects on high-efficiency InGaP/InGaAs/Ge triple-junction solar cells developed for terrestrial use”. In: *Conference record of the 29th IEEE Photovoltaic Specialists Conference*. 2002, pp. 990–993.
- [Ima+03] M. Imaizumi, T. Takamoto, T. Sumita, T. Ohshima, M. Yamaguchi, S. Matsuda, A. Ohi, and T. Kamiya. “Study of radiation response on single-junction component sub-cells in triple-junction solar cells”. In: *3rd World Conference on Photovoltaic Energy Conversion, 2003. Proceedings of 1* (2003).
- [Ima+16] Mitsuru Imaizumi, Tetsuya Nakamura, Tatsuya Takamoto, Takeshi Ohshima, and Michio Tajima. “Radiation degradation characteristics of component subcells in inverted metamorphic triple-junction solar cells irradiated with electrons and protons”. In: *Progress in Photovoltaics: Research and Applications* (2016). DOI: 10.1002/pip.2840.
- [Jac+07] David B. Jackrel, Seth R. Bank, Homan B. Yuen, Mark a. Wistey, James S. Harris, Aaron J. Ptak, Steven W. Johnston, Daniel J. Friedman, and Sarah R. Kurtz. “Dilute nitride GaInNAs and GaInNAsSb solar cells by molecular beam epitaxy”. In: *Journal of Applied Physics* 101.11 (2007), pp. 1–8. DOI: 10.1063/1.2744490.
- [Jak+12] Roberto Jakomin, Antonella Parisini, Luciano Tarricone, Massimo Longo, Beatrice Fraboni, and Salvatore Vantaggio. *On the electrical properties of Si-doped InGaP layers grown by low pressure-metalorganic vapor phase epitaxy*. 2012. DOI: 10.1016/j.tsf.2012.07.009.
- [Jia+06] C.-s. Jiang, D. Friedman, H. Moutinho, and M.m. Al-Jassim. “Profiling the Built-In Electrical Potential in III-V Multijunction Solar Cells”. In: *2006 IEEE 4th World Conference on Photovoltaic Energy Conference*. IEEE, 2006, pp. 853–856. DOI: 10.1109/WCPEC.2006.279591.
- [Jia+16] Jieyang Jia, Zheng Lyu, Mengyang Yuan, Yusi Chen, Yijie Huo, Taner Bilir, Yu Miao, Muyu Xue, James S Harris, Solar Junction, and San Jose. “Accurate Characterization of Luminescent Coupling Effects with Voltage and Light Bias Adjustment”. In: *2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC), Portland, OR* (2016), pp. 1224–1228. DOI: 10.1109/PVSC.2016.7749809.
- [Jon+13] Rebecca Jones-Albertus et al. “Using Dilute Nitrides to Achieve Record Solar Cell Efficiencies”. In: *MRS Proceedings* 1538 (2013), pp. 161–166. DOI: 10.1557/opl.2013.656.
- [JR91] S.C. Jain and D.J. Roulston. “A simple expression for band gap narrowing (BGN) in heavily doped Si, Ge, GaAs and GexSi1-x strained layers”. In: *Solid-State Electronics* 34.5 (May 1991), pp. 453–465. DOI: 10.1016/0038-1101(91)90149-S.

- [Kal+10] N. A. Kalyuzhnyy, A. S. Gudovskikh, V. V. Evstropov, V. M. Lantratov, S. A. Mintairov, N. Kh. Timoshina, M. Z. Shvarts, and V. M. Andreev. “Germanium subcells for multijunction GaInP/GaInAs/Ge solar cells”. In: *Semiconductors* 44.11 (2010), pp. 1520–1528. DOI: 10.1134/S106378261011028X.
- [Kat+94] Hirokazu Kato, Sadao Adachi, Hiroshi Nakanishi, and Kouji Ohtsuka. “Optical Properties of $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ Quaternary Alloys”. In: *Japanese Journal of Applied Physics* 33.Part 1, No.1A (Jan. 1994), pp. 186–192. DOI: 10.1143/JJAP.33.186.
- [Kay+11] Brendan M. Kayes, Hui Nie, Rose Twist, Sylvia G. Spruytte, Frank Reinhardt, Isik C. Kizilyalli, and Gregg S. Higashi. “27.6% Conversion efficiency, a new record for single-junction solar cells under 1 sun illumination”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference* (2011), pp. 000004–000008. DOI: 10.1109/PVSC.2011.6185831.
- [KF97] F.A. Kish and R.M. Fletcher. “Chapter 5 AlGaInP Light-Emitting Diodes”. In: *Semiconductors and Semimetals* 48 (1997), pp. 149–C3. DOI: 10.1016/S0080-8784(08)62406-0.
- [KFO90] Sarah R. Kurtz, P. Faine, and J. M. Olson. “Modeling of two-junction, series-connected tandem solar cells using top-cell thickness as an adjustable parameter”. In: *Journal of Applied Physics* 68.4 (1990), pp. 1890–1895. DOI: 10.1063/1.347177.
- [KFS17] S A Kozhukhovskaia, E D Filimonov, and M Z Shvarts. “Optical leakage versus luminescent coupling in a multijunction solar cell: how to recognize a source of additional photocurrent in subcells”. In: *Journal of Physics: Conference Series* 816.1 (Mar. 2017), p. 012040. DOI: 10.1088/1742-6596/816/1/012040.
- [Kin+08] Geoffrey S. Kinsey, Peter Hebert, Kent E. Barbour, Dmitri D. Krut, Hector L. Cotal, and Raed A. Sherif. “Concentrator multijunction solar cell characteristics under variable intensity and temperature”. In: *Progress in Photovoltaics: Research and Applications* 16.6 (Sept. 2008), pp. 503–508. DOI: 10.1002/pip.834.
- [Kin+11] R. R. King, D. Bhusari, A. Boca, D. Larrabee, X.-Q. Liu, W. Hong, C. M. Fetzer, D. C. Law, and N. H. Karam. “Band gap-voltage offset and energy production in next-generation multijunction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 19.7 (Nov. 2011), pp. 797–812. DOI: 10.1002/pip.1044.
- [Kir+08] Thomas Kirchartz, Uwe Rau, Martin Hermle, Andreas W. Bett, Anke Helbig, and Jürgen H. Werner. “Internal voltages in GaIn/PGaInAs/Ge multijunction solar cells determined by electroluminescence measurements”. In: *Applied Physics Letters* 92.12 (2008), pp. 90–93. DOI: 10.1063/1.2903101.

- [KLR15] Kang Min Kim, Jung Il Lee, and Jeong Ho Ryu. “Thermal annealing effect on nitrogen related defects of GaInNAs semiconductors”. In: *Journal of Ceramic Processing Research* 16.1 (2015), pp. 45–48.
- [KOM10] Ana Kanevce, Jerry M. Olson, and Wyatt K. Metzger. “Numerical simulations of triple-junction GaInP/GaAs/Ge solar cells to provide insight into fill-factor losses at high concentration”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference* (2010), pp. 2066–2069. DOI: 10.1109/PVSC.2010.5616586.
- [Kon+96] Masahiko Kondow, Kazuhisa Uomi, Atsuko Niwa, Takeshi Kitatani, Seiji Watahiki, and Yoshiaki Yazawa. “GaInNAs: A novel material for long-wavelength-range laser diodes with excellent high-temperature performance”. In: *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers* 35.2 SUPPL. B (1996), pp. 1273–1275. DOI: 10.1143/JJAP.35.1273.
- [Kor+07] Omer Korech, Baruch Hirsch, Eugene a. Katz, and Jeffrey M. Gordon. “High-flux characterization of ultrasmall multijunction concentrator solar cells”. In: *Applied Physics Letters* 91.6 (2007), pp. 2–4. DOI: 10.1063/1.2766666.
- [Kos+16] A. Kosa, L. Stuchlikova, L. Harmatha, M. Mikolasek, J. Kovac, B. Sciana, W. Dawidowski, D. Radziewicz, and M. Tlaczala. “Defect distribution in InGaAsN/GaAs multilayer solar cells”. In: *Solar Energy* 132 (2016), pp. 587–590. DOI: 10.1016/j.solener.2016.03.057.
- [Kri+02] P. Krispin, V. Gambin, J. S. Harris, and K. H. Ploog. “Ga(As,N) layers in the dilute N limit studied by depth-resolved capacitance spectroscopy”. In: *Applied Physics Letters* 81.21 (Nov. 2002), pp. 3987–3989. DOI: 10.1063/1.1522823.
- [Kri+03] P. Krispin, V. Gambin, J. S. Harris, and K. H. Ploog. “Nitrogen-related electron traps in Ga(As,N) layers ($\approx \frac{1}{2}$ 3% N)”. In: *Journal of Applied Physics* 93.10 (May 2003), pp. 6095–6099. DOI: 10.1063/1.1568523.
- [KS02] Charalambos C Katsidis and Dimitrios I Siapkas. “General transfer-matrix method for optical multilayer systems with coherent, partially coherent, and incoherent interference.” In: *Applied optics* 41.19 (2002), pp. 3978–3987. DOI: 10.1364/AO.41.003978.
- [Kuo+97] H. C. Kuo, J. M. Kuo, Y. C. Wang, C. H. Lin, H. Chen, and G. E. Stillman. “Determination of the Band Offset of GaInP- GaAs and AlInP- GaAs Quantum Wells by Optical Spectroscopy”. In: *Journal of Electronic Materials* 26.8 (1997), pp. 944–948. DOI: 10.1007/s11664-997-0279-1.

- [Kur+00] Sarah Kurtz, J. F. Geisz, D. J. Friedman, J. M. Olson, A. Duda, N. H. Karam, R. R. King, J. H. Ermer, and D. E. Joslin. “Modeling of electron diffusion length in GaInAsN solar cells”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference 2000-Janua* (2000), pp. 1210–1213. DOI: 10.1109/PVSC.2000.916106.
- [Kur+02a] Steven R. Kurtz, J. F. Klem, A. A. Allerman, R. M. Sieg, C. H. Seager, and E. D. Jones. “Minority carrier diffusion and defects in InGaAsN grown by molecular beam epitaxy”. In: *Applied Physics Letters* 80.8 (Feb. 2002), pp. 1379–1381. DOI: 10.1063/1.1453480.
- [Kur+02b] Steven R Kurtz, Normand A Modine, Eric D Jones, Andrew A Allerman, and John F Klem. “Insights into the electronic properties of InGaAsN: the effect of nitrogen from band structure to devices”. In: *Semiconductor Science and Technology* 17.8 (Aug. 2002), pp. 843–850. DOI: 10.1088/0268-1242/17/8/313.
- [Kur+04] Sarah Kurtz, J. F. Geisz, D. J. Friedman, W. K. Metzger, R. R. King, and N. H. Karam. “Annealing-induced-type conversion of GaInNAs”. In: *Journal of Applied Physics* 95.5 (Mar. 2004), pp. 2505–2508. DOI: 10.1063/1.1643775.
- [Kur+13] Sarah Kurtz, Richard King, Daniel Law, Aaron Ptak, John Geisz, and Nasser Karam. “Effects of in situ annealing on GaInNAs solar cells”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference*. IEEE, June 2013, pp. 2095–2099. DOI: 10.1109/PVSC.2013.6744887.
- [Kur+99] Sarah R. Kurtz, J. M. Olson, D. J. Friedman, J. F. Geisz, K. a. Bertness, and a. E. Kibbler. “Passivation of Interfaces in High-Efficiency Photovoltaic Devices”. In: *MRS Proceedings* 573.May (1999), p. 95. DOI: 10.1557/PROC-573-95.
- [Lan+15a] Dongchen Lan, John F. Geisz, Myles A. Steiner, Ivan Garcia, Daniel J. Friedman, and Martin A. Green. “Improved modeling of photoluminescent and electroluminescent coupling in multijunction solar cells”. In: *Solar Energy Materials and Solar Cells* 143 (Dec. 2015), pp. 48–51. DOI: 10.1016/j.solmat.2015.06.036.
- [Lan+15b] Fabian Langer, Svenja Perl, Sven Höfling, and Martin Kamp. “P- to n-type conductivity transition in 1.0 eV GaInNAs solar cells controlled by the V/III ratio”. In: *Applied Physics Letters* 106.6 (Feb. 2015), p. 063905. DOI: 10.1063/1.4909507.
- [LB89] Jeremiah R. Lowney and Herbert S. Bennett. *Effects of doping-density gradients on band-gap narrowing in silicon and GaAs devices*. 1989. DOI: 10.1063/1.343215.
- [Lee+12] Wooyoung Lee, Seung-Yeol Lee, Jungho Kim, Sung Chul Kim, and Byoungho Lee. “A numerical analysis of the effect of partially-coherent light in photovoltaic devices considering coherence length”. In: *Optics Express* 20.S6 (2012), A941. DOI: 10.1364/OE.20.00A941.

- [Lee+93] H. Lee, M. V. Klein, D. E. Aspnes, C. P. Kuo, M. Peanasky, and M. G. Craford. “Optical study of (Al x Ga 1-completely disordered x) 0.5 In 0.5 P/GaAs semiconductor alloys by spectroscopic ellipsometry”. In: *Journal of Applied Physics* 73.1 (1993), pp. 400–406. DOI: 10.1063/1.354046.
- [Leo+16] Nelvin Leong, Kian Hua Tan, Wan Khai Loke, Satrio Wicaksono, Daosheng Li, Soon Fatt Yoon, Prithu Sharma, Tim Milakovich, Mayank Bulsara, and Gene Fitzgerald. “Growth of 1-eV GaNAsSb-based photovoltaic cell on silicon substrate at different As/Ga beam equivalent pressure ratios”. In: *Progress in Photovoltaics: Research and Applications* 24.3 (Mar. 2016), pp. 340–347. DOI: 10.1002/pip.2705. arXiv: 1303.4604.
- [LH10] Antonio Luque and Steven Hegedus, eds. *Handbook of Photovoltaic Science and Engineering*. Chichester, UK: John Wiley & Sons, Ltd, Dec. 2010. DOI: 10.1002/9780470974704.
- [LHB06] G. Létay, M. Hermle, and a. W. Bett. “Simulating single-junction GaAs solar cells including photon recycling”. In: *Progress in Photovoltaics: Research and Applications* 14.8 (2006), pp. 683–696. DOI: 10.1002/pip.699.
- [Li+08] Z.M. Q. Li, Y. G. Xiao, M. Lestrade, and Z.M. M.Simon Li. “2D-simulation of inverted metamorphic GaInP/GaAs/GaInAs triple junction solar cell”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference*. IEEE, May 2008, pp. 1–6. DOI: 10.1109/PVSC.2008.4922475.
- [Li+13] Jing-Jing Li, Charles R. Allen, Swee Hoe Lim, and Yong-Hang Zhang. “Elimination of Artifacts in External Quantum Efficiency Measurements of Multijunction Solar Cells Using a Pulsed Voltage Bias”. In: *IEEE Journal of Photovoltaics* 3.2 (Apr. 2013), pp. 769–775. DOI: 10.1109/JPHOTOV.2013.2242959.
- [Lim+13] Swee Hoe Lim, Jing-Jing Li, Elizabeth H. Steenbergen, and Yong-Hang Zhang. “Luminescence coupling effects on multijunction solar cell external quantum efficiency measurement”. In: *Progress in Photovoltaics: Research and Applications* 21.3 (2013), pp. 344–350. DOI: 10.1002/pip.1215.
- [Liu+93] W. Liu, T. Henderson, E. Beam, and S.-K. Fan. “Electron saturation velocity in Ga0.5InP0.5P measured in a GaInP/GaAs/GaInP double-heterojunction bipolar transistor”. In: *Electronics Letters* 29.21 (1993), p. 1885. DOI: 10.1049/el:19931255.
- [LLJ79] D. V. Lang, R. a. Logan, and M. Jaros. “Trapping characteristics and a donor-complex (DX) model for the persistent-photoconductivity trapping center in Te-doped AlxGa1-xAs”. In: *Physical Review B* 19.2 (1979), pp. 1015–1030. DOI: 10.1103/PhysRevB.19.1015.

- [LLK77] D. V. Lang, R. A. Logan, and L. C. Kimerling. “Identification of the defect state associated with a gallium vacancy in GaAs and Al_xGa_{1-x}As”. In: *Physical Review B* 15.10 (1977), pp. 4874–4882. DOI: 10.1103/PhysRevB.15.4874.
- [LNC07] Lan Luo, Guofu Niu, and John D. Cressler. “Modeling of bandgap narrowing for consistent simulation of SiGe HBTs across a wide temperature range”. In: *Proceedings of the IEEE Bipolar/BiCMOS Circuits and Technology Meeting* (2007), pp. 123–126. DOI: 10.1109/BIPOL.2007.4351851.
- [Lom+17] I. Lombardero, M. Ochoa, I. García, M. Hinojosa, P. Caño, I. Rey-Stolle, C. Algora, A. Johnson, J. I. Davies, K. H. Tan, W. K. Loke, S. Wicaksono, S. F. Yoon, R. Romero, and M. Gabás. “Preliminary analysis of annealing impact on 1 eV GaNAsSb Solar Cells”. In: *Spanish Conference on Electron Devices (CDE)*. Barcelona, Spain, 2017.
- [Lov+92] M. L. Lovejoy, M. R. Melloch, M. S. Lundstrom, and R. K. Ahrenkiel. “Minority hole mobility in n+GaAs”. In: *Applied Physics Letters* 61.22 (Nov. 1992), pp. 2683–2684. DOI: 10.1063/1.108108.
- [LRS96] M. Levinstein, S. Rumyantsev, and M. Shur. *Handbook Series on Semiconductor Parameters. volume 2*. World Scientific, 1996. DOI: 10.1142/9789812832085_fmatter.
- [LS82] M. S. Lundstrom and R. J. Schuelke. “Modeling semiconductor heterojunctions in equilibrium”. In: *Solid State Electronics* 25.8 (1982), pp. 683–691. DOI: 10.1016/0038-1101(82)90195-2.
- [LS83] Mark S. Lundstrom and Robert John Schuelke. “Numerical Analysis of Heterostructure Semiconductor Devices”. In: *IEEE Transactions on Electron Devices* 30.9 (Sept. 1983), pp. 1151–1159. DOI: 10.1109/T-ED.1983.21271.
- [Lum+14] Matthew P. Lumb, Myles A. Steiner, John F. Geisz, and Robert J. Walters. “Incorporating photon recycling into the analytical drift-diffusion model of high efficiency solar cells”. In: *Journal of Applied Physics* 116.19 (Nov. 2014), p. 194504. DOI: 10.1063/1.4902320.
- [Lun+90] M. S. Lundstrom, M. E. Klausmeier-Brown, M. R. Melloch, R. K. Ahrenkiel, and B. M. Keyes. “Device-related material properties of heavily doped gallium arsenide”. In: *Solid State Electronics* 33.6 (1990), pp. 693–704. DOI: 10.1016/0038-1101(90)90182-E.
- [Lun06] Mark Lundstrom. *ECE 612 Lecture 31: Heterostructure Fundamentals*. Dec. 2006.
- [Luo+02] H.T Luo, W.Z Shen, Y.H Zhang, and H.F Yang. “Study of band gap narrowing effect in n-GaAs for the application of far-infrared detection”. In: *Physica B: Condensed Matter* 324.1-4 (Nov. 2002), pp. 379–386. DOI: 10.1016/S0921-4526(02)01428-X.

- [Lus09] G. B. Lush. “B-coefficient in n-type GaAs”. In: *Solar Energy Materials and Solar Cells* 93.8 (2009), pp. 1225–1229. DOI: 10.1016/j.solmat.2009.01.020.
- [LXL06] Z Q Li, Y G Xiao, and Z M Simon Li. “Modeling of multi-junction solar cells by Crosslight APSYS”. In: *Proc of SPIE Vol 6339* (2006), pp. 633909–633909–8. DOI: 10.1117/12.681258.
- [LXL07] Z. Q. Li, Y. G. Xiao, and Z. M. Simon Li. “Two-dimensional simulation of GaInP/-GaAs/Ge triple junction solar cell”. In: *Physica Status Solidi (C)* 4.5 (2007), pp. 1637–1640. DOI: 10.1002/pssc.200674271.
- [MAO15] Naoya Miyashita, Nazmul Ahsan, and Yoshitaka Okada. “Characterization of 1.0 eV GaInNAsSb solar cells for multijunction applications and the effect of annealing”. In: *Proc. 31st European Photovoltaic Solar Energy Conference and Exhibition (EU-PVSEC)*. Hamburg, 2015, pp. 1461–1465.
- [MAO16a] Naoya Miyashita, Nazmul Ahsan, and Yoshitaka Okada. “Generation and collection of photocarriers in dilute nitride GaInNAsSb solar cells”. In: *Progress in Photovoltaics: Research and Applications* 24.1 (June 2016), pp. 28–37. DOI: 10.1002/pip.2641.
- [MAO16b] Naoya Miyashita, Nazmul Ahsan, and Yoshitaka Okada. “Improvement of 1.0 eV GaInNAsSb solar cell performance upon annealing”. In: *2016 Compound Semiconductor Week (CSW) [Includes 28th International Conference on Indium Phosphide & Related Materials (IPRM) & 43rd International Symposium on Compound Semiconductors (ISCS)*. IEEE, June 2016, pp. 1–1. DOI: 10.1109/ICIPRM.2016.7528760.
- [MAO17] Naoya Miyashita, Nazmul Ahsan, and Yoshitaka Okada. “Improvement of 1.0 eV GaInNAsSb solar cell performance upon optimal annealing”. In: *physica status solidi (a)* 214.3 (Mar. 2017), p. 1600586. DOI: 10.1002/pssa.201600586.
- [Max+13] S. I. Maximenko, S. R. Messenger, R. Hoheisel, D. Scheiman, M. Gonzalez, J. Lorentzen, P. P. Jenkins, and R. J. Walters. “Characterization of high fluence irradiations on advanced triple junction solar cells”. In: *Conference Record of the 39th IEEE Photovoltaic Specialists Conference*. 2013, pp. 2797–2800. DOI: 10.1109/PVSC.2013.6745053.
- [MBR97] A. Martí, J. L. Balenzategui, and R.F. Reyna. “Photon recycling and Shockley’s diode equation”. In: *Journal of Applied Physics* 82.8 (1997), pp. 4067–4075. DOI: 10.1063/1.365717.
- [McM+08] W. E. McMahon, K. E. Emery, D. J. Friedman, L. Ottoson, M. S. Young, J. S. Ward, C. M. Kramer, A. Duda, and Sarah Kurtz. “Fill factor as a probe of current-matching for GaInP₂/GaAs tandem cells in a concentrator system during outdoor operation”. In: *Progress in Photovoltaics: Research and Applications* 16.3 (May 2008), pp. 213–224. DOI: 10.1002/pip.798.

- [Mel13] Alexander Mellor. “Photon Management Structures for Absorption Enhancement in Intermediate Band Solar Cells and Crystalline Silicon Solar Cells”. PhD thesis. IES-UPM, 2013.
- [Mes+01] S. R. Messenger, G. P. Summers, E. A. Burke, R. J. Walters, and M. A. Xapsos. “Modeling solar cell degradation in space: A comparison of the NRL displacement damage dose and the JPL equivalent fluence approaches”. In: *Progress in Photovoltaics: Research and Applications* 9.2 (Mar. 2001), pp. 103–121. DOI: 10.1002/pip.357.
- [Mes+13] S. R. Messenger, R. Hoheisel, J. Lorentzen, D. Scheiman, J. H. Warner, M. Gonzalez, and P. P. Jenkins. “High fluence irradiations on triple junction solar cells”. English. In: *2013 IEEE 39th Photovoltaic Specialists Conference (PVSC)*. IEEE, June 2013, pp. 3121–3127. DOI: 10.1109/PVSC.2013.6745120.
- [Meu+03] M. Meusel, C. Baur, G. Lütz, A.W. Bett, W. Warta, and E. Fernandez. “Spectral response measurements of monolithic GaInP/Ga(In)As/Ge triple-junction solar cells: Measurement artifacts and their explanation”. In: *Progress in Photovoltaics: Research and Applications* 11.8 (Dec. 2003), pp. 499–514. DOI: 10.1002/pip.514.
- [MFG17] William E. McMahon, Daniel J. Friedman, and John F. Geisz. “Multijunction solar cell design revisited: disruption of current matching by atmospheric absorption bands”. In: *Progress in Photovoltaics: Research and Applications* (May 2017). DOI: 10.1002/pip.2899.
- [MFL16] T Masuda, J Faucher, and M L Lee. “Molecular beam epitaxy growth of germanium junctions for multi-junction solar cell applications”. In: *Journal of Physics D: Applied Physics* 49.46 (2016), p. 465105. DOI: 10.1088/0022-3727/49/46/465105.
- [MM93] B. Mazhari and H. Morkoç. “Surface recombination in GaAs PN junction diode”. In: *Journal of Applied Physics* 73.11 (June 1993), pp. 7509–7514. DOI: 10.1063/1.353998.
- [Mön01] W Mönch. *Semiconductor surfaces and interfaces*. Vol. 26. Springer, 2001.
- [MYK12] Owen D Miller, Eli Yablonovitch, and Sarah R Kurtz. “intense internal and external fluorescence as solar cell approach the SQ efficiency limit”. In: *Photovoltaics, IEEE Journal of* 2.3 (2012), pp. 1–27. DOI: 10.1109/JPHOTOV.2012.2198434.
- [Nak+12] Tetsuya Nakamura, Mitsuru Imaizumi, Shin-ichiro Sato, and Takeshi Ohshima. “Change in I-V characteristics of subcells in a multi-junction solar cell due to radiation irradiation”. In: *Conference Record of the 38th IEEE Photovoltaic Specialists Conference*. 2012, pp. 2486–2850.

- [Nes+15] H Nesswetter, N R Jost, P Lugli, A W Bett, and C G Zimmermann. “Determination of subcell I-V parameters by a pulsed suns-Voc method including optical coupling”. In: *Applied Physics Letters* 106.2 (2015). DOI: 10.1063/1.4906237.
- [Nie+17] M. Niemeyer, J. Ohlmann, A. W. Walker, P. Kleinschmidt, R. Lang, T. Hannappel, F. Dimroth, and D. Lackner. “Minority carrier diffusion length, lifetime and mobility in p-type GaAs and GaInAs”. In: *Journal of Applied Physics* 122.11 (2017), p. 115702. DOI: 10.1063/1.5002630.
- [Nis+06] Kensuke Nishioka, Tatsuya Takamoto, Takaaki Agui, Minoru Kaneiwa, Yukiharu Uraoka, and Takashi Fuyuki. “Evaluation of InGaP/InGaAs/Ge triple-junction solar cell and optimization of solar cell’s structure focusing on series resistance for high-efficiency concentrator photovoltaic systems”. In: *Solar Energy Materials and Solar Cells* 90.9 (May 2006), pp. 1308–1321. DOI: 10.1016/j.solmat.2005.08.003.
- [NSM15] Milos Nedeljkovic, Richard Soref, and Goran Z. Mashanovich. “Predictions of Free-Carrier Electroabsorption and Electrorefraction in Germanium”. In: *IEEE Photonics Journal* 7.3 (June 2015), pp. 1–14. DOI: 10.1109/JPHOT.2015.2419217.
- [NTA86] S. Nojima, H. Tanaka, and H. Asahi. “Deep electron trapping center in Si-doped InGaAlP grown by molecular-beam epitaxy”. In: *Journal of Applied Physics* 59.10 (May 1986), p. 3489. DOI: 10.1063/1.336819.
- [Och+14] M. Ochoa, C. Algora, P. Espinet-González, and I. García. “3-D modeling of perimeter recombination in GaAs diodes and its influence on concentrator solar cells”. In: *Solar Energy Materials and Solar Cells* 120 (2014), pp. 48–58. DOI: 10.1016/j.solmat.2013.08.009.
- [Och+16b] M. Ochoa, M. A. Steiner, I. García, J. F. Geisz, D. J. Friedman, and C. Algora. “Influence of temperature on luminescent coupling and material quality evaluation in inverted lattice-matched and metamorphic multi-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 24.3 (Mar. 2016), pp. 357–367. DOI: 10.1002/pip.2714.
- [Och+16c] M. Ochoa et al. “Advances towards 4J lattice-matched including dilute nitride subcell for terrestrial and space applications”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference*. Vol. 2016-Novem. IEEE, June 2016, pp. 52–57. DOI: 10.1109/PVSC.2016.7749407.
- [Och+16d] Mario Ochoa, Iván García, Iván Lombardero, Luna Ayllón, Ignacio Rey-Stolle, Carlos Algora, Andrew Johnson, J. Iwan Davies, Kian Hua Tan, Wan Khai Loke, Satrio Wicaksono, Soon Fatt Yoon, Efraín Ochoa-Martínez, and Mercedes Gabás. “Modelling of lattice matched dilute nitride 4-junction concentrator solar cells on Ge substrates”. In: *AIP Con-*

- ference Proceedings*. Vol. 1766. 1. AIP Publishing, 2016, p. 080003. DOI: 10.1063/1.4962101.
- [Och+17] M. Ochoa, E. Yacuzzi, P. Espinet-González, M. Barrera, E. Barrigón, M. L. Ibarra, Yedileth Contreras, J. García, E. López, M. Alurralde, C. Algora, E. Godfrin, I. Rey-Stolle, and J. Plá. “10 MeV proton irradiation effects on GaInP/GaAs/Ge concentrator solar cells and their component subcells”. In: *Solar Energy Materials and Solar Cells* 159 (2017), pp. 576–582. DOI: 10.1016/j.solmat.2016.09.042.
- [Och+18] E. Ochoa-Martínez, L. Barrutia, M. Ochoa, E. Barrigón, I. García, I. Rey-Stolle, C. Algora, P. Basa, G. Kronome, and M. Gabás. “Refractive indexes and extinction coefficients of n- and p-type doped GaInP, AlInP and AlGaInP for multijunction solar cells”. In: *Solar Energy Materials and Solar Cells* 174. April 2017 (2018), pp. 388–396. DOI: 10.1016/j.solmat.2017.09.028.
- [Ohs+06] Takeshi Ohshima, Haruki Miyamoto, Mitsuru Imaizumi, Chiharu Morioka, Shirou Kawakita, Kazunori Shimazaki, Koichi Kibe, Katsuyasu Kawano, and Hisayoshi Itoh. “Current Injection Effects on the Electrical Performance of 3J Solar Cells Irradiated with Low and High Energy Protons”. In: *Conference Record of the 4th World Conference on Photovoltaic Energy Conversion*. 2006, pp. 1818–1821.
- [Ols+89] J.M. Olson, R.K. Ahrenkiel, D.J. Dunlavy, Brian Keyes, and a.E. Kibbler. “Ultralow recombination velocity at GaInP/GaAs heterointerfaces”. In: *Applied Physics Letters* 55 (1989), p. 1208.
- [Ols10] J. M. Olson. “Simulation of nonuniform irradiance in multijunction III-V solar cells”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference* (2010), pp. 201–204. DOI: 10.1109/PVSC.2010.5614523.
- [OMK07] J. M. Olson, W. E. McMahon, and Sarah Kurtz. “Effect of Sb on the properties of GaInP top cells”. In: *Conference Record of the 2006 IEEE 4th World Conference on Photovoltaic Energy Conversion, WCPEC-4*. Vol. 1. IEEE, 2007, pp. 787–790. DOI: 10.1109/WCPEC.2006.279574.
- [OMO02] A. Ohmae, N. Matsumoto, and Y. Okada. “Growth of GaInNAs by atomic hydrogen-assisted RF-MBE”. In: *MBE 2002-2002 12th International Conference on Molecular Beam Epitaxy*. IEEE, 2002, pp. 271–272. DOI: 10.1109/MBE.2002.1037864.
- [ONe04] Mark J. O’Neill. “1,000 W/kg Solar Concentrator Arrays for Far-Term Space Missions”. In: *AIP Conference Proceedings*. Vol. 699. 1. AIP, Feb. 2004, pp. 875–882. DOI: 10.1063/1.1649652.

- [OSK11] J. M. Olson, M. A. Steiner, and A. Kanevce. “Using measurements of fill factor at high irradiance to deduce heterobarrier band offsets”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference* July (2011), pp. 003754–003757. DOI: 10.1109/PVSC.2011.6186459.
- [Ost+] C.R. Osterwald, K.A. Emery, D.R. Myers, and R.E. Hart. “Primary reference cell calibrations, at SERI: history and methods”. In: *IEEE Conference on Photovoltaic Specialists*. IEEE, pp. 1062–1067. DOI: 10.1109/PVSC.1990.1111780.
- [Ost+14a] C R Osterwald, M W Wanlass, T Moriarty, M A Steiner, and K A Emery. “Concentrator Cell Efficiency Measurement Errors Caused by Unfiltered Xenon Flash Solar Simulators Concentrator Cell Efficiency Measurement Errors Caused by Unfiltered Xenon Flash Solar Simulators”. In: *AIP Conference Proceedings* 1616.APRIL (2014), pp. 149–153.
- [Ost+14b] C R Osterwald, M W Wanlass, T Moriarty, M A Steiner, and K A Emery. “Concentrator Cell Efficiency Measurement Errors Caused by Unfiltered Xenon Flash Solar Simulators Concentrator Cell Efficiency Measurement Errors Caused by Unfiltered Xenon Flash Solar Simulators”. In: *AIP Conference Proceedings* 1616.APRIL (2014), pp. 149–153.
- [Ost+14c] C R Osterwald, M W Wanlass, T Moriarty, M A Steiner, and K A Emery. “Effects of Spectral Error in Efficiency Measurements of GaInAs-Based Concentrator Solar Cells Effects of Spectral Error in Efficiency Measurements of GaInAs-Based Concentrator Solar Cells”. In: March (2014).
- [Pal85] Edward D. Palik. “Gallium Arsenide (GaAs)”. In: *Handbook of Optical Constants of Solids*. Ed. by EDWARD D PALIK. Boston: Academic Press, 1985, pp. 429–443. DOI: <http://dx.doi.org/10.1016/B978-0-08-054721-3.50020-4>.
- [Pal97] E.D. Palik. *Handbook of Optical Constants of Solids*. Elsevier, 1997, pp. 403–423. DOI: 10.1016/B978-012544415-6.50109-6.
- [Pan71] J. I. Pankove. *Optical Processes in Semiconductors*. Dover, 1971.
- [PBS97] Joseph W. Parks, Kevin F. Brennan, and Arlynn W. Smith. “Two-dimensional model of photon recycling in direct gap semiconductor devices”. In: *Journal of Applied Physics* 82.7 (1997), pp. 3493–3498. DOI: 10.1063/1.365622.
- [Per+14] Emmett E. Perl, Chieh Ting Lin, William E. McMahon, Daniel J. Friedman, and John E. Bowers. “Ultrabroadband and wide-angle hybrid antireflection coatings with nanostructures”. In: *IEEE Journal of Photovoltaics* 4.3 (2014), pp. 962–967. DOI: 10.1109/JPHOTOV.2014.2304359.

- [Per+15] Emmett E. Perl, John Simon, John F. Geisz, Waldo Olavarria, Michelle Young, Anna Duda, Pat Dippo, Daniel J. Friedman, and Myles A. Steiner. “Development of a 2.0 eV AlGaInP solar cell grown by OMVPE”. English. In: *2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC)*. IEEE, June 2015, pp. 1–6. DOI: 10.1109/PVSC.2015.7356336.
- [Per+16] Emmett E Perl, John Simon, John F Geisz, Waldo Olavarria, Michelle Young, Anna Duda, Daniel J. Friedman, and Myles A Steiner. “Development of High - Bandgap AlGaInP Solar Cells Grown by Organometallic Vapor - Phase Epitaxy”. In: *IEEE Journal of Photovoltaics* 6.3 (2016), pp. 770–776. DOI: 10.1109/JPHOTOV.2016.2537543.
- [Per+17] E. E. Perl, D. Kuciauskas, J. Simon, D. J. Friedman, and M. A. Steiner. “Identification of the limiting factors for high-temperature GaAs, GaInP, and AlGaInP solar cells from device and carrier lifetime analysis”. In: *Journal of Applied Physics* 122.23 (2017). DOI: 10.1063/1.5003631.
- [PFJ02] A J Ptak, D J Friedman, and S W Johnston. “A comparison of MBE- and MOCVD-grown InGaAsN”. In: *MBE 2002 - 2002 12th International Conference on Molecular Beam Epitaxy* 251 (2002), pp. 291–292. DOI: 10.1109/MBE.2002.1037874.
- [PFK07] A. J. Ptak, D. J. Friedman, and Sarah Kurtz. “Effects of temperature, nitrogen ions, and antimony on wide depletion width GaInNAs”. In: *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 25.3 (2007), p. 955. DOI: 10.1116/1.2715993.
- [Phi+08] Sp Philipps, M Hemle, G Letay, and W Guter. “Numerical Simulation and Modeling of III-V Multi-Junction Solar Cells”. In: ... *Photovoltaic Solar Energy* ... September (2008), pp. 1–5.
- [Phi+15] Simon P. Philipps, Andreas W. Bett, Kelsey Horowitz, and Sarah Kurtz. “Current Status of Concentrator Photovoltaic (CPV) Technology”. In: *National Renewable Energy Laboratory* (2015), pp. 1–25. DOI: <http://www.ise.fraunhofer.de/en/publications/veroeffentlichungen-pdf-dateien-en/studien-und-konzeptpapiere/current-status-of-concentrator-photovoltaic-cpv-technology.pdf>.
- [Plu08] Solar Probe Plus: *Report of the Science and Technology Definition Team*. Tech. rep. 2008.
- [Pol+16a] Ville Polojärvi, Arto Aho, Antti Tukiainen, Marianna Raappana, Timo Aho, Andreas Schramm, and Mircea Guina. “Influence of As/group-III flux ratio on defects formation and photovoltaic performance of GaInNAs solar cells”. In: *Solar Energy Materials and Solar Cells* 149 (2016), pp. 213–220. DOI: 10.1016/j.solmat.2016.01.024.

- [Pol+16b] Ville Polojärvi, Arto Aho, Antti Tukiainen, Andreas Schramm, and Mircea Guina. “Comparative study of defect levels in GaInNAs, GaNAsSb, and GaInNAsSb for high-efficiency solar cells”. In: *Applied Physics Letters* 108.12 (2016), p. 122104. DOI: 10.1063/1.4944844.
- [Pot85] ROY F. Potter. “Germanium (Ge)”. In: *Handbook of Optical Constants of Solids*. Ed. by EDWARD D PALIK. Boston: Academic Press, 1985, pp. 465–478. DOI: <http://dx.doi.org/10.1016/B978-0-08-054721-3.50022-8>.
- [Pra01a] Ignacio Rey-Stolle Prado. “Desarrollo de Células Solares de GaAs para Concentraciones Luminosas Muy Elevadas”. PhD thesis. IES-UPM, 2001, pp. 44–87.
- [Pra01b] Ignacio Rey-Stolle Prado. “Desarrollo de Células Solares de GaAs para Concentraciones Luminosas Muy Elevadas.” PhD thesis. Universidad Politécnica de Madrid, 2001.
- [Pre] Press Release: NREL. “NREL Demonstrates 45.7% Efficiency for Concentrator Solar Cells”. DOI: <https://www.nrel.gov/news/press/2014/15436.html>.
- [Pre00] J S C Prentice. “Coherent, partially coherent and incoherent light absorption in thin-film multilayer structures”. In: *Journal of Physics D: Applied Physics* 33.24 (2000), pp. 3139–3145. DOI: 10.1088/0022-3727/33/24/302.
- [Pre99] J S C Prentice. “Optical generation rate of electron-hole pairs in multilayer thin-film photovoltaic cells”. In: *Journal of Physics D: Applied Physics* 32.17 (1999), pp. 2146–2150. DOI: 10.1088/0022-3727/32/17/302.
- [Pri53] M. B. Prince. “Drift Mobilities in Semiconductors. I. Germanium”. In: *Physical Review B* 92.3 (1953), pp. 681–687.
- [Pta+03] a J Ptak, S Kurtz, S W Johnston, D J Friedman, J F Geisz, and J M Olson. “Defects in GaInNAs: What We’ve Learned So Far”. In: *NCPV and Solar Program Review Meeting Proceedings* May (2003), pp. 202–205.
- [Pta+04] A J Ptak, Sarah Kurtz, M H Weber, and K G Lynn. “Positron annihilation study of vacancies in GaInNAs”. In: *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures* 22.3 (2004), p. 1584. DOI: 10.1116/1.1752914.
- [Pta+05] A J Ptak, D J Friedman, Sarah Kurtz, and R C Reedy. “Low-acceptor-concentration GaInNAs grown by molecular-beam epitaxy for high-current p-i-n solar cell applications”. In: *Journal of Applied Physics* 98.9 (2005). DOI: 10.1063/1.2113414.
- [Rau07] Uwe Rau. “Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells”. In: *Physical Review B - Condensed Matter and Materials Physics* 76.8 (2007), pp. 1–8. DOI: 10.1103/PhysRevB.76.085303.

- [Ren+15] Zekun Ren, Jonathan P. Mailoa, Zhe Liu, Haohui Liu, Sin Cheng Siah, Tonio Buonassisi, and Ian Marius Peters. “Numerical Analysis of Radiative Recombination and Reabsorption in GaAs/Si Tandem”. In: *IEEE Journal of Photovoltaics* 5.4 (2015), pp. 1079–1086. DOI: 10.1109/JPHOTOV.2015.2427580.
- [Rod+14] P. Rodrigo, E.F. Fernández, F. Almonacid, and P.J. Pérez-Higueras. “Review of methods for the calculation of cell temperature in high concentration photovoltaic modules for electrical characterization”. In: *Renewable and Sustainable Energy Reviews* 38 (2014), pp. 478–488. DOI: 10.1016/j.rser.2014.06.008.
- [RYH95] K. C. Reinhardt, Y. K. Yeo, and R. L. Hengehold. “Junction characteristics of Ga_{0.5}In_{0.5}P n +p diodes and solar cells”. In: *Journal of Applied Physics* 77.11 (1995), pp. 5763–5772. DOI: 10.1063/1.359221.
- [Sat+09a] Shin Ichiro Sato, Haruki Miyamoto, Mitsuru Imaizumi, Kazunori Shimazaki, Chiharu Morioka, Katsuyasu Kawano, and Takeshi Ohshima. “Degradation modeling of InGaP/-GaAs/Ge triple-junction solar cells irradiated with various-energy protons”. In: *Solar Energy Materials and Solar Cells* 93.6-7 (2009), pp. 768–773. DOI: 10.1016/j.solmat.2008.09.044.
- [Sat+09b] Shin ichiro Sato, Haruki Miyamoto, Mitsuru Imaizumi, Kazunori Shimazaki, Chiharu Morioka, Katsuyasu Kawano, and Takeshi Ohshima. “Degradation modeling of InGaP/-GaAs/Ge triple-junction solar cells irradiated with various-energy protons”. In: *Solar Energy Materials and Solar Cells*. Ed. by Alexandre Freundlich and Jean-François Guillemoles. Vol. 93. 6-7. International Society for Optics and Photonics, Mar. 2009, pp. 768–773. DOI: 10.1016/j.solmat.2008.09.044.
- [SB14] Gerald Siefer and Andreas W. Bett. “Analysis of temperature coefficients for III-V multi-junction concentrator cells”. In: *Progress in Photovoltaics: Research and Applications* 22.5 (May 2014), pp. 515–524. DOI: 10.1002/pip.2285.
- [Sch+13] F. J. Schultes, T. Christian, R. Jones-Albertus, E. Pickett, K. Alberi, B. Fluegel, T. Liu, P. Misra, a. Sukiasyan, H. Yuen, and N. M. Haegel. “Temperature dependence of diffusion length, lifetime and minority electron mobility in GaInP”. In: *Applied Physics Letters* 103.24 (2013), pp. 1–5. DOI: 10.1063/1.4847635.
- [Sch+95] Mathias Schubert, Craig M Herzinger, Huacie Yao, Paul G Snyder, and John a Woollam. “Optical constants”. In: 77.7 (1995), pp. 6–9.
- [Sch05] Dieter K. Schroder. *Semiconductor Material and Device Characterization: Third Edition*. Hoboken, NJ, USA: John Wiley & Sons, Inc., Oct. 2005, pp. 1–779. DOI: 10.1002/0471749095. arXiv: 0408133v1 [arXiv:cond-mat].

- [Sch06] E. Fred. Schubert. *Light-emitting diodes*. Cambridge University Press, 2006, p. 422.
- [Sch98] Andreas Schenk. *Advanced Physical Models for Silicon Device Simulation*. 1998.
- [SEA12] Matthew T. Sheldon, Carissa N. Eisler, and Harry a. Atwater. “GaAs passivation with trioctylphosphine sulfide for enhanced solar cell efficiency and durability”. In: *Advanced Energy Materials* 2.3 (2012), pp. 339–344. DOI: 10.1002/aenm.201100666.
- [Sel84] Siegfried Selberherr. “The Discretization of the Basic Semiconductor Equations”. In: *Analysis and Simulation of Semiconductor Devices* (1984), pp. 149–201. DOI: 10.1007/978-3-7091-8752-4_6.
- [SG12] Myles A. Steiner and John F Geisz. “Non-linear luminescent coupling in series-connected multijunction solar cells Non-linear luminescent coupling in series-connected multijunction solar cells”. In: *Applied Physics Letters* 100 (2012), p. 251106. DOI: 10.1063/1.4729827.
- [Sha+04] W Shan, K M Yu, W Walukiewicz, J Wu, J W Ager, and E E Haller. “Band anticrossing in dilute nitrides”. In: *Journal of Physics: Condensed Matter* 16.31 (2004), S3355–S3372. DOI: 10.1088/0953-8984/16/31/024.
- [Sha+17] P Sharps et al. “Next Generation Radiation Hard IMM Space Solar Cells”. In: *11th European Space Power Conference*. Vol. 16. 2017, p. 03002. DOI: 10.1051/e3sconf/20171603002.
- [Sha+99] W. Shan, W. Walukiewicz, J. W. Ager, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz. “Band anticrossing in GaInNAs alloys”. In: *Physical Review Letters* 82.6 (1999), pp. 1221–1224. DOI: 10.1103/PhysRevLett.82.1221.
- [Shi+03] Yun Shi, Guofu Niu, John D. Cressler, and David L. Hareme. “On the consistent modeling of band-gap narrowing for accurate device-level simulation of scaled SiGe HBTs”. In: *IEEE Transactions on Electron Devices* 50.5 (2003), pp. 1370–1377. DOI: 10.1109/TED.2003.813237.
- [Shv+13] M. Z. Shvarts, M. A. Mintairov, V. M. Emelyanov, V. V. Evstropov, V. M. Lantratov, and N. Kh Timoshina. “Method for direct measurements of luminescent coupling efficiency in concentrator MJ SCs”. In: *AIP Conference Proceedings* 1556.812 (2013), pp. 147–151. DOI: 10.1063/1.4822219.
- [Shv+15] Maxim Shvarts, Viktor Emelyanov, Mikhail Mintairov, Valery Evstropov, and Nailya Timoshina. “Temperature influence on luminescent coupling efficiency in concentrator MJ SCs”. In: *AIP Conference Proceedings* 1679 (2015). DOI: 10.1063/1.4931560.

- [Shv+16] Maxim Z Shvarts, Viktor M Emelyanov, Valery V Evstropov, Mikhail A Mintairov, Evgeniy D Filimonov, and Svetlana A Kozhukhovskaia. “Overcoming the Luminescent Coupling Effect in Experimental Search for the True Quantum Efficiency Values in Multi-Junction Solar Cells”. In: *AIP Conference Proceedings 1766* 060005 (2016), pp. 1–6. DOI: <http://dx.doi.org/10.1063/1.4962095>.
- [Sil12a] Silvaco. *Atlas user’s manual*. Silvaco, 2012.
- [Sil12b] Silvaco. *Deckbuild user’s manual*. Silvaco, 2012.
- [Sil16] Silvaco. *Atlas User’s Manual*. 2016.
- [SN06] S.M. Sze and Kwok K. Ng. *Physics of Semiconductor Devices*. Hoboken, NJ, USA: John Wiley & Sons, Inc., Oct. 2006.
- [SNN99] R. Sakamoto, K. Nakata, and S. Nakajima. “High-field electron transport in GaInP”. In: *Physica B: Condensed Matter* 272.1-4 (1999), pp. 250–252. DOI: 10.1016/S0921-4526(99)00428-7.
- [Sog+13] Tomah Sogabe, Akio Ogura, Chao Yu Hung, Valery Evstropov, Mikhail Mintairov, Maxim Shvarts, and Yoshitaka Okada. “Experimental characterization and self-consistent modeling of luminescence coupling effect in III-V multijunction solar cells”. In: *Applied Physics Letters* 103.26 (2013), pp. 4–6. DOI: 10.1063/1.4858970.
- [SOI09] Shin Ichiro Sato, Takeshi Ohshima, and Mitsuru Imaizumi. “Modeling of degradation behavior of InGaP/GaAs/Ge triple-junction space solar cell exposed to charged particles”. In: *Journal of Applied Physics* 105.4 (2009). DOI: 10.1063/1.3079522.
- [Sot+00] M Sotoodeh, A H Khalid, A A Rezazadeh, P Additionally, and I Introduction. “Empirical low-field mobility model for III-V compounds applicable in device simulation codes”. In: *Journal of Applied Physics* 87.6 (2000), pp. 2890–2900.
- [Spe] Spectrolab Web. www.spectrolab.com/DataSheets/PV/CPV/C4MJ_40_Percent_Solar_Cell.pdf.
- [SR52] W. Shockley and W. T. Read. *Statistics of the Recombination of Holes and Electrons*. 1952. DOI: dx.doi.org/10.1103/PhysRev.87.835.
- [ST71] J G Simmons and G W Taylor. “Nonequilibrium Steady-State Statistics and Associated Effects for Insulators and Semiconductors Containing an Arbitrary Distribution of Traps”. In: *Phys. Rev. B* 4.2 (July 1971), pp. 502–511. DOI: 10.1103/PhysRevB.4.502.
- [Sta+02] M.A. Stan, D.J. Aiken, P.R. Sharps, N.S. Fatemi, F.A. Spadafora, J. Hills, H. Yoo, and B. Clevenger. “27.5% efficiency InGaP/InGaAs/Ge advanced triple junction (ATJ) space solar cells for high volume manufacturing”. In: *Conference Record of the Twenty-Ninth IEEE Photovoltaic Specialists Conference, 2002*. IEEE, 2002, pp. 816–819. DOI: 10.1109/PVSC.2002.1190700.

- [Ste+11] Myles A. Steiner, John F. Geisz, Daniel J. Friedman, Waldo J. Olavarria, Anna Duda, and Tom E. Moriarty. “Temperature-dependent measurements of an inverted metamorphic multijunction (IMM) solar cell”. In: *2011 37th IEEE Photovoltaic Specialists Conference*. IEEE, June 2011, pp. 002527–002532. DOI: 10.1109/PVSC.2011.6186461.
- [Ste+13a] M. A. Steiner, J. F. Geisz, I. García, D. J. Friedman, A. Duda, and S. R. Kurtz. “Optical enhancement of the open-circuit voltage in high quality GaAs solar cells”. In: *Journal of Applied Physics* 113.12 (2013), p. 123109. DOI: 10.1063/1.4798267.
- [Ste+13b] Myles A. Steiner, John F. Geisz, Ivan Garcia, Daniel J. Friedman, Anna Duda, Waldo J. Olavarria, Michelle Young, Darius Kuciauskas, and Sarah R. Kurtz. “Effects of internal luminescence and internal optics on Voc and Jsc of III-V solar cells”. In: *IEEE Journal of Photovoltaics* 3.4 (2013), pp. 1437–1442. DOI: 10.1109/JPHOTOV.2013.2278666.
- [Ste+13c] Myles A. Steiner, John F. Geisz, Tom E. Moriarty, Ryan M. France, William E. McMahon, Jerry M. Olson, Sarah R. Kurtz, and Daniel J. Friedman. “Measuring IV curves and subcell photocurrents in the presence of luminescent coupling”. In: *IEEE Journal of Photovoltaics* 3.2 (2013), pp. 879–887. DOI: 10.1109/JPHOTOV.2012.2228298.
- [Ste+15] Myles A Steiner, Matthew P Lumb, Raymond Hoheisel, John F Geisz, Ryan M France, David Scheiman, Robert J Walters, and Phillip P Jenkins. “Radiation effects on luminescent coupling in III-V solar cells”. In: *2015 IEEE 42nd Photovoltaic Specialist Conference, PVSC 2015*. 2015. DOI: 10.1109/PVSC.2015.7355672.
- [Ste+16] E Sterzer, A Beyer, L Nattermann, W Schorn, K Schlechter, S Pulz, J Sundermeyer, W Stolz, and K Volz. “Novel nitrogen/gallium precursor [Ga(bdma)H₂] for MOVPE”. In: *Journal of Crystal Growth* 454 (2016), pp. 173–179. DOI: 10.1016/j.jcrysgro.2016.08.061.
- [Ste+90a] T B Stellwag, M R Melloch, M S Lundstrom, M S Carpenter, and R F Pierret. “Orientation-dependent perimeter recombination in {GaAs} diodes”. In: *Applied physics letters* 56.17 (1990), pp. 1658–1660.
- [Ste+90b] T. B. Stellwag, M. R. Melloch, M. S. Lundstrom, M. S. Carpenter, and R. F. Pierret. *Orientation-dependent perimeter recombination in GaAs diodes*. 1990. DOI: 10.1063/1.103108.
- [Sto+99] S. A. Stockman, J. -W. Huang, T. D. Osentowski, H. C. Chui, M. J. Peanasky, S. A. Maranowski, P. N. Grillo, A. J. Moll, C. H. Chen, C. P. Kuo, and B. W. Liang. “Oxygen incorporation in AlInP, and its effect on P-type doping with magnesium”. In: *Journal of Electronic Materials* 28.7 (July 1999), pp. 916–925. DOI: 10.1007/s11664-999-0220-x.

- [Str+00] G. B. Stringfellow, R. T. Lee, C. M. Fetzter, J. K. Shurtleff, Yu Hsu, S. W. Jun, S. Lee, and T. Y. Seong. “Surfactant effects of dopants on ordering in GaInP”. In: *Journal of Electronic Materials* 29.1 (2000), pp. 134–139. DOI: 10.1007/s11664-000-0108-2.
- [Str02] G. B. Stringfellow. “Effects of the Surface on CuPt Ordering During OMVPE Growth”. In: *Spontaneous Ordering in Semiconductor Alloys*. Boston, MA: Springer US, 2002, pp. 99–117. DOI: 10.1007/978-1-4615-0631-7_3.
- [Sua+17] F. Suarez, T. Liu, A. Sukiasyan, J. Lang, E. Pickett, E. Lucow, T. Bilir, S. Chary, R. Roucka, I. Aeby, L. Zhang, and S. Siala. “Advances in Dilute Nitride Multi-Junction solar cells for space power applications”. In: *E3S Web of Conferences* 16, 03006. 2017.
- [Sum+03] T. Sumita, M. Imaizumi, S. Matsuda, T. Ohshima, A. Ohi, and H. Itoh. “Proton radiation analysis of multi-junction space solar cells”. In: *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 206 (May 2003), pp. 448–451. DOI: 10.1016/S0168-583X(03)00791-2.
- [Sum+94] G.P. Summers, R.J. Walters, M.A. Xapsos, E.A. Burke, S.R. Messenger, P. Shapiro, and R.L. Statler. “A new approach to damage prediction for solar cells exposed to different radiations”. In: *Proceedings of 1994 IEEE 1st World Conference on Photovoltaic Energy Conversion - WCPEC (A Joint Conference of PVSC, PVSEC and PSEC)* 2 (1994), pp. 2068–2075. DOI: 10.1109/WCPEC.1994.521828.
- [SYW12] Vijit Sabnis, Homan Yuen, and Mike Wiemer. “High-efficiency multijunction solar cells employing dilute nitrides”. In: *AIP Conference Proceedings* 1477 (2012), pp. 14–19. DOI: 10.1063/1.4753823.
- [Sze81] S M Sze. *Physics of semiconductor devices*. 1981.
- [Tan+11] K.H. Tan, S. Wicaksono, W.K. Loke, D. Li, S.F. Yoon, E.A. Fitzgerald, S.A. Ringel, and J.S. Harris Jr. “Molecular beam epitaxy grown GaNAsSb 1eV photovoltaic cell”. In: *Journal of Crystal Growth* 335.1 (Nov. 2011), pp. 66–69. DOI: 10.1016/j.jcrysgro.2011.09.023.
- [TFW88] Sandip Tiwari, D J Frank, and Steven L Wright. “Surface recombination in {GaAlAs/-GaAs} heterostructure bipolar transistors”. In: *Journal of Applied Physics* 64.10 (1988), pp. 5009–5012. DOI: 10.1063/1.342452.
- [TGV66] J. Tauc, R. Grigorovici, and A. Vancu. “Optical Properties and Electronic Structure of Amorphous Germanium”. In: *physica status solidi (b)* 15.2 (Jan. 1966), pp. 627–637. DOI: 10.1002/pssb.19660150224.

- [TH66] D. G. Thomas and J. J. Hopfield. “Isoelectronic Traps Due to Nitrogen in Gallium Phosphide”. In: *Physical Review* 150.2 (Oct. 1966), pp. 680–689. DOI: 10.1103/PhysRev.150.680.
- [Tho+14] Tomos Thomas, Markus Fuhrer, Diego Alonso Alvarez, Ned Ekins-Daukes, Kian Hua Tan, Satrio Wicaksono, Wan Khai Loke, Soon Fatt Yoon, and Andrew Johnson. “GaNAsSb 1-eV solar cells for use in lattice-matched multi-junction architectures”. In: *Conference record of the 40th IEEE Photovoltaic Specialists Conference*. IEEE, June 2014, pp. 0550–0553. DOI: 10.1109/PVSC.2014.6924980.
- [Tom93] Kazutaka Tomizawa. *Numerical Simulation of Submicron Semiconductor Devices*. Artech House, 1993, p. 356.
- [Tro+10] M Claudia Troparevsky, Adrian S Sabau, Andrew R Lupini, and Zhenyu Zhang. “Transfer-matrix formalism for the calculation of optical response in multilayer systems: from coherent to incoherent interference.” In: *Optics express* 18.24 (2010), pp. 24715–24721. DOI: 10.1364/OE.18.024715.
- [Tuk+16] A. Tukiainen, A. Aho, V. Polojärvi, R. Ahorinta, and M. Guina. “High efficiency dilute nitride solar cells: Simulations meet experiments”. In: *Journal of Green Engineering* 5.3-4 (2016), pp. 113–132. DOI: 10.13052/jge1904-4720.5348.
- [Tur+13] Marek Turowski, Timothy Bald, Ashok Raman, Alex Fedoseyev, Jeffrey H. Warner, Cory D. Cress, and Robert J. Walters. “Simulating the radiation response of GaAs solar cells using a defect-based TCAD model”. In: *IEEE Transactions on Nuclear Science* 60.4 (2013), pp. 2477–2485. DOI: 10.1109/TNS.2013.2273446.
- [TW90] Sandip Tiwari and Steven L. Wright. “Material properties of p-type GaAs at large dopings”. In: *Applied Physics Letters* 56.6 (1990), pp. 563–565. DOI: 10.1063/1.102745.
- [Vai+16] Michelle Vaisman, Kunal Mukherjee, Taizo Masuda, Kevin Nay Yaung, Eugene A. Fitzgerald, and Minjoo Larry Lee. “Direct-Gap 2.1-2.2 eV AlInP Solar Cells on GaInAs/-GaAs Metamorphic Buffers”. In: *IEEE Journal of Photovoltaics* 6.2 (Mar. 2016), pp. 571–577. DOI: 10.1109/JPHOTOV.2015.2506401.
- [Van50] W. Van Roosbroeck. “Theory of the Flow of Electrons and Holes in Germanium and Other Semiconductors”. In: *Bell System Technical Journal* 29.4 (Oct. 1950), pp. 560–607. DOI: 10.1002/j.1538-7305.1950.tb03653.x.
- [VG02] Dragica Vasileska and Stephen M. Goodnick. *Computational electronics*. Vol. 38. 5. 2002, pp. 181–236. DOI: 10.1016/S0927-796X(02)00039-6.

- [VHG10] Alexis Vossier, Baruch Hirsch, and Jeffrey M. Gordon. “Is Auger recombination the ultimate performance limiter in concentrator solar cells?” In: *Applied Physics Letters* 97.19 (2010), pp. 30–32. DOI: 10.1063/1.3510474.
- [VM03] I. Vurgaftman and J. R. Meyer. “Band parameters for nitrogen-containing semiconductors”. In: *Journal of Applied Physics* 94.6 (2003), pp. 3675–3696. DOI: 10.1063/1.1600519.
- [VMR01] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan. “Band parameters for III-V compound semiconductors and their alloys”. In: *Journal of Applied Physics* 89.11 I (2001), pp. 5815–5875. DOI: 10.1063/1.1368156.
- [Vol+08] K. Volz, D. Lackner, I. Németh, B. Kunert, W. Stolz, C. Baur, F. Dimroth, and A. W. Bett. “Optimization of annealing conditions of (GaIn)(NAs) for solar cell applications”. In: *Journal of Crystal Growth* 310.7-9 (2008), pp. 2222–2228. DOI: 10.1016/j.jcrysgro.2007.11.199.
- [Vol+09] Kerstin Volz, Jörg Koch, Falko Höhnsdorf, Bernardette Kunert, and Wolfgang Stolz. “MOVPE growth of dilute nitride III/V semiconductors using all liquid metalorganic precursors”. In: *Journal of Crystal Growth* 311.8 (Apr. 2009), pp. 2418–2426. DOI: 10.1016/j.jcrysgro.2008.09.210.
- [VR07] M. P. Vaughan and B. K. Ridley. “The Hall Mobility in Dilute Nitrides”. In: *Dilute III-V Nitride Semiconductors and Material Systems*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2007. Chap. 10, pp. 255–281. DOI: 10.1007/978-3-540-74529-7_10.
- [Wal+05] R.J. Walters, J.H. Warner, G.P. Summers, S.R. Messenger, and J.R. Lorentzen. “Radiation response mechanisms in multijunction III-V space solar cells”. In: *Conference Record of the 31st IEEE Photovoltaic Specialists Conference*. IEEE, 2005, pp. 542–547. DOI: 10.1109/PVSC.2005.1488188.
- [Wal+14] A W Walker, F Bouchard, A H Trojnar, and K Hinzer. “Inverted Metamorphic III - V Triple-Junction Solar Cell with a 1 eV CuInSe₂ Bottom Subcell”. In: 2014.001 (2014). DOI: 10.1155/2014/913170.
- [Wal+15] Alexandre W. Walker, Oliver Höhn, Daniel Neves Micha, Benedikt Bläsi, Andreas W. Bett, and Frank Dimroth. “Impact of Photon Recycling on GaAs Solar Cell Designs”. In: *IEEE Journal of Photovoltaics* 5.6 (2015), pp. 1636–1645. DOI: 10.1109/JPHOTOV.2015.2479463.
- [Wal+16] A. W. Walker, S. Heckelmann, C. Karcher, O. Höhn, C. Went, M. Niemeyer, A. W. Bett, and D. Lackner. “Nonradiative lifetime extraction using power-dependent relative photoluminescence of III-V semiconductor double-heterostructures”. In: *Journal of Applied Physics* 119.15 (Apr. 2016), p. 155702. DOI: 10.1063/1.4945772.

- [War+04] Jeffrey H. Warner, Robert J. Walters, Scott R. Messenger, Geoffrey P. Summers, Shyam M. Khanna, Diego Estan, Lorne S. Erhardt, and Alain Houdayer. “High-energy proton irradiation effects in GaAs devices”. In: *IEEE Transactions on Nuclear Science* 51.5 III (2004), pp. 2887–2895. DOI: 10.1109/TNS.2004.835071.
- [War+10] J.H. Warner, C.D. Cress, S.R. Messenger, R.J. Walters, S. A. Ringel, and J. Park. “A Deep Level Transient Spectroscopy Study of Electron and Proton Irradiated p+n GaAs Diodes”. In: *IEEE Transactions on Nuclear Science* 57.4 (2010), pp. 282–285. DOI: 10.1109/TNS.2010.2046335.
- [WCW15] Uli Wurfel, Andres Cuevas, and Peter Wurfel. “Charge Carrier Separation in Solar Cells”. In: *IEEE Journal of Photovoltaics* 5.1 (Jan. 2015), pp. 461–469. DOI: 10.1109/JPHOTOV.2014.2363550.
- [Web] Webpage Solar Junction. http://www.sj-solar.com/about_us/space.php.
- [Whe+09] Jeffrey F. Wheeldon, Christopher E. Valdivia, Alex Walker, Gitanjali Kolhatkar, Trevor J. Hall, Karin Hinzer, Denis Masson, Simon Fafard, Abdelatif Jaouad, Artur Turala, Richard Arés, and Vincent Aimez. “AlGaAs tunnel junction for high efficiency multi-junction solar cells: Simulation and measurement of temperature-dependent operation”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference* 1 (2009), pp. 000106–000111. DOI: 10.1109/PVSC.2009.5411723.
- [Wic+05] S. Wicaksono, S.F. Yoon, W.J. Fan, and W.K. Loke. “The effect of rapid thermal annealing on GaAsSbN quantum-well and GaAsSbN bulk lattice matched to GaAs”. In: *International Conference on Indium Phosphide and Related Materials, 2005*. IEEE, 2005, pp. 421–423. DOI: 10.1109/ICIPRM.2005.1517518.
- [Wil+13] Matthew Wilkins, Alex Walker, Jeffrey F. Wheeldon, Gilbert Arbez, Henry Schriemer, and Karin Hinzer. “Design constraints of n-p InGaAsN dilute nitride sub-cells for 3- and 4- junction solar cell applications under concentrated illumination”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference*. IEEE, June 2013, pp. 2139–2143. DOI: 10.1109/PVSC.2013.6744897.
- [Wil+14] Matthew M Wilkins, Ahmed M Gabr, Anna H Trojnar, Henry Schriemer, and Karin Hinzer. “Effects of Luminescent Coupling in Single- and 4-Junction Dilute Nitride Solar Cells”. In: *2014 IEEE 40th Photovoltaic Specialist Conference (PVSC)* (2014), pp. 3601–3604. DOI: 10.1109/PVSC.2014.6924885.
- [Wil+15] Matthew Wilkins, Christopher E. Valdivia, Ahmed M. Gabr, Denis Masson, Simon Fafard, and Karin Hinzer. “Luminescent coupling in planar opto-electronic devices”. In: *Journal of Applied Physics* 118.14 (Oct. 2015), p. 143102. DOI: 10.1063/1.4932660.

- [Wil+16] Matthew Wilkins, James Gupta, Simon Fafard, Abdelatif Jaouad, Boussairi Bouzazi, Abderraouf Boucherif, Christopher E. Valdivia, Richard Arès, Vincent Aimez, Henry P. Schriemer, and Karin Hinzer. “Design of InGaAsN(Sb) p-i-n junctions for use in 4-junction concentrating photovoltaic devices”. In: *Journal of Photonics for Energy* 7.2 (2016), pp. 3–6. DOI: 10.1117/1.JPE.7.022502.
- [WNS77] M. Wolf, G.T. Noel, and R.J. Stirn. “Investigation of the double exponential in the current-voltage characteristics of silicon solar cells”. In: *IEEE Transactions on Electron Devices* 24.4 (Apr. 1977), pp. 419–428. DOI: 10.1109/T-ED.1977.18750.
- [WO87] Miyoko O. Watanabe and Yasuo Ohba. “Interface properties for GaAs/InGaAlP heterojunctions by the capacitance-voltage profiling technique”. In: *Applied Physics Letters* 50.14 (1987), pp. 906–908. DOI: 10.1063/1.98028.
- [Wol+85] D. J. Wolford, J. A. Bradley, K. Fry, and J. Thompson. “The Nitrogen Isoelectronic Trap in GaAs”. In: *Proceedings of the 17th International Conference on the Physics of Semiconductors*. New York, NY: Springer New York, 1985, pp. 627–630. DOI: 10.1007/978-1-4615-7682-2_138.
- [WS93] Markus Weyers and Michio Sato. “Growth of GaAsN alloys by low-pressure metalorganic chemical vapor deposition using plasma-cracked NH₃”. In: *Applied Physics Letters* 62.12 (Mar. 1993), pp. 1396–1398. DOI: 10.1063/1.108691.
- [WSA92] Markus Weyers, Michio Sato, and Hiroaki Ando. “Red shift of photoluminescence and absorption in dilute GaAsN alloy layers”. In: *Japanese Journal of Applied Physics* 31.7 (July 1992), pp. L853–L855. DOI: 10.1143/JJAP.31.L853.
- [WSM00] R.J. Walters, G.P. Summers, and S.R. Messenger. “Analysis and modeling of the radiation response of multijunction space solar cells”. In: *Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference - 2000 (Cat. No.00CH37036)*. IEEE, 2000, pp. 1092–1097. DOI: 10.1109/PVSC.2000.916077.
- [WW16] Peter Wurfel and Uli Wurfel. *Physics of solar cells : from basic principles to advanced concepts*. Third. Wiley, 2016, p. 113. DOI: 10.
- [YEH93] Kyoungsoon Yang, Jack R. East, and George I. Haddad. “Numerical modeling of abrupt heterojunctions using a thermionic-field emission boundary condition”. In: *Solid-State Electronics* 36.3 (1993), pp. 321–330. DOI: 10.1016/0038-1101(93)90083-3.
- [YH13] Wangqing Yuan and D. C. Hall. “Variable-angle spectroscopic ellipsometry of InAlP native oxide dielectric layers for GaAs metal-oxide-semiconductor field effect transistor applications”. In: *Journal of Applied Physics* 113.10 (2013). DOI: 10.1063/1.4794817.

- [YHD02] M. Yee, P. a. Houston, and J. P. R. David. “Measurement of electron saturation velocity in Ga_{0.52}In_{0.48}P in a double heterojunction bipolar transistor”. In: *Journal of Applied Physics* 91.3 (2002), p. 1601. DOI: 10.1063/1.1428100.
- [Yi+09] Wei Yi, Hong Lu, Yong Huang, Michael A Scarpulla, Jae-Hyun Ryou, Arthur C Gossard, Russell D Dupuis, and Venkatesh Narayanamurti. “Bandgap and Band Offsets Determination of Semiconductor Heterostructures using Three-terminal Ballistic Carrier Spectroscopy”. In: (2009). arXiv: arXiv:0904.2364v1.
- [Yoo+05] H. Yoon, K.M. Edmondson, G.S. Kinsey, R.R. King, P. Hebert, R.K. Ahrenkiel, B.T. Cavicchi, and N.H. Karam. “Minority carrier lifetime and radiation damage coefficients of germanium”. In: *Conference Record of the Thirty-first IEEE Photovoltaic Specialists Conference, 2005*. IEEE, 2005, pp. 842–845. DOI: 10.1109/PVSC.2005.1488264.
- [Yua+16] Mengyang Yuan, Zheng Lyu, Jieyang Jia, Yusi Chen, Yi Liu, Yijie Huo, Yu Miao, and James Harris. “Numerical modeling of photon recycling and luminescence coupling in non-ideal multijunction solar cell”. In: *Proc. SPIE 9743, Physics, Simulation, and Photonic Engineering of Photovoltaic Devices V* (2016), p. 974306. DOI: 10.1117/12.2213362.
- [Yue+06] Homan B. Yuen, Seth R. Bank, Hopil Bae, Mark A. Wistey, and James S. Harris. “The role of antimony on properties of widely varying GaInNAsSb compositions”. In: *Journal of Applied Physics* 99.9 (2006), pp. 1–8. DOI: 10.1063/1.2191745.
- [Yue06] H.B. Yuen. “Growth and characterization of dilute nitride antimonides for long-wavelength optoelectronics”. PhD thesis. Stanford University, 2006.
- [ZAI81] He-Zhong Zhu, Yoshio Adachi, and Toshiaki Ikoma. “Deep levels in MOCVD GaAs grown under different Ga/As mol fractions”. In: *Journal of Crystal Growth* 55.1 (Oct. 1981), pp. 154–163. DOI: 10.1016/0022-0248(81)90283-9.
- [ZCF98] X. H. Zhang, S. J. Chua, and W. J. Fan. “Band offsets at GaInP/AlGaInP(001) heterostructures lattice matched to GaAs”. In: *Applied Physics Letters* 73.8 (Aug. 1998), p. 1098. DOI: 10.1063/1.122096.
- [ZS91] Xiumiao Zhang and Jiatao Song. “The effect of surface recombination on surface photovoltage in semiconductors”. In: *Journal of Applied Physics* 70.8 (1991), pp. 4632–4633. DOI: 10.1063/1.349074.

Publications

Journal Publications

- [1] Enrique Barrigón, Mario Ochoa, Ivan García, Laura Barrutia, Carlos Algora, and Ignacio Rey-Stolle. “Degradation of Ge subcells by thermal load during the growth of multijunction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 26.2 (2018), pp. 102–111. DOI: 10.1002/pip.2948.
- [2] E. Ochoa-Martínez, L. Barrutia, M. Ochoa, E. Barrigón, I. García, I. Rey-Stolle, C. Algora, P. Basa, G. Kronome, and M. Gabás. “Refractive indexes and extinction coefficients of n- and p-type doped GaInP, AlInP and AlGaInP for multijunction solar cells”. In: *Solar Energy Materials and Solar Cells* 174. April 2017 (2018), pp. 388–396. DOI: 10.1016/j.solmat.2017.09.028.
- [3] Ivan García, Mario Ochoa, Iván Lombardero, Luis Cifuentes, Manuel Hinojosa, Pablo Caño, Ignacio Rey-Stolle, Carlos Algora, Andrew Johnson, Iwan Davies, Kian Hua Tan, Wan Khai Loke, Satrio Wicaksono, and Soon Fatt Yoon. “Degradation of subcells and tunnel junctions during growth of GaInP/Ga(In)As/GaNAsSb/Ge 4-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 25.11 (Sept. 2017), pp. 887–895. DOI: 10.1002/pip.2930.
- [4] M. Ochoa, E. Yaccuzzi, P. Espinet-González, M. Barrera, E. Barrigón, M. L. Ibarra, Yedileth Contreras, J. García, E. López, M. Alurralde, C. Algora, E. Godfrin, I. Rey-Stolle, and J. Plá. “10 MeV proton irradiation effects on GaInP/GaAs/Ge concentrator solar cells and their component subcells”. In: *Solar Energy Materials and Solar Cells* 159 (2017), pp. 576–582. DOI: 10.1016/j.solmat.2016.09.042.

- [5] E. Barrigón, L. Barrutia, M. Ochoa, I. Rey-Stolle, and Carlos Algora. “Effect of Sb on the quantum efficiency of GaInP solar cells”. In: *Prog. Photovolt: Res. Appl.* 24 (2016), pp. 1116–1122. DOI: 10.1002/pip.2777.
- [6] D. Fuertes Marrón, E. Barrigón, M. Ochoa, and I. Artacho. “Quantitative Determination of Luminescent Coupling in Multijunction Solar Cells from Spectral Photovoltage Measurements”. In: *Physical Review Applied* 6.1 (2016), pp. 1–6. DOI: 10.1103/PhysRevApplied.6.014001.
- [7] M. Ochoa, E. Barrigón, L. Barrutia, I. García, I. Rey-Stolle, and C. Algora. “Limiting factors on the semiconductor structure of III-V multijunction solar cells for ultra-high concentration (1000–5000 suns)”. In: *Progress in Photovoltaics: Research and Applications* 24.10 (2016), pp. 1332–1345. DOI: 10.1002/pip.2791.
- [8] M. Ochoa, M. A. Steiner, I. García, J. F. Geisz, D. J. Friedman, and C. Algora. “Influence of temperature on luminescent coupling and material quality evaluation in inverted lattice-matched and metamorphic multi-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 24.3 (Mar. 2016), pp. 357–367. DOI: 10.1002/pip.2714.
- [9] P Espinet-González, I Rey-Stolle, M Ochoa, C Algora, I García, and E Barrigón. “Analysis of perimeter recombination in the subcells of GaInP/GaAs/Ge triple-junction solar cells”. In: *Progress in Photovoltaics: Research and Applications* 23.7 (2015), pp. 874–882. DOI: 10.1002/pip.2501.
- [10] I García, J F Geisz, R M France, J Kang, S-H Wei, M Ochoa, and D J Friedman. “Metamorphic Ga_{0.76}In_{0.24}As/GaAs_{0.75}Sb_{0.25} tunnel junctions grown on GaAs substrates”. In: *Journal of Applied Physics* 116.7 (2014), p. 74508.
- [11] M. Ochoa, C. Algora, P. Espinet-González, and I. García. “3-D modeling of perimeter recombination in GaAs diodes and its influence on concentrator solar cells”. In: *Solar Energy Materials and Solar Cells* 120 (2014), pp. 48–58. DOI: 10.1016/j.solmat.2013.08.009.

Conference Publications

- [12] I. García, M. Ochoa, I. Lombardero, L. Cifuentes, P. Caño, M. Hinojosa, I. Rey-Stolle, C. Algora, A. D. Johnson, J. I. Davies, K.H. Tan, W.K. Loke, S. Wicaksono, and S.F. Yoon. “Component Integration Effects in 4-junction Solar Cells with Dilute Nitride 1eV Subcell”. In: IEEE 44th Photovoltaic Specialists Conference (PVSC), 2017, To be published.

- [13] I. Lombardero, M. Ochoa, I. García, M. Hinojosa, P. Caño, I. Rey-Stolle, C. Algora, A. Johnson, J. I. Davies, K. H. Tan, W. K. Loke, S. Wicaksono, S. F. Yoon, R. Romero, and M. Gabás. “Preliminary analysis of annealing impact on 1 eV GaNAsSb Solar Cells”. In: *Spanish Conference on Electron Devices (CDE)*. Barcelona, Spain, 2017.
- [14] Ignacio Rey-Stolle, Iván García, Enrique Barrigón, Javier Olea, David Pastor, Mario Ochoa, Laura Barrutia, Carlos Algora, and Wladek Walukiewicz. “On the thermal degradation of tunnel diodes in multijunction solar cells”. In: *AIP Conference Proceedings*. Vol. 1881. 2017, p. 040005. DOI: 10.1063/1.5001427.
- [15] M. Ochoa et al. “Advances towards 4J lattice-matched including dilute nitride subcell for terrestrial and space applications”. In: *Conference Record of the IEEE Photovoltaic Specialists Conference*. Vol. 2016-Novem. IEEE, June 2016, pp. 52–57. DOI: 10.1109/PVSC.2016.7749407.
- [16] Mario Ochoa, Iván García, Iván Lombardero, Luna Ayllón, Ignacio Rey-Stolle, Carlos Algora, Andrew Johnson, J. Iwan Davies, Kian Hua Tan, Wan Khai Loke, Satrio Wicaksono, Soon Fatt Yoon, Efraín Ochoa-Martínez, and Mercedes Gabás. “Modelling of lattice matched dilute nitride 4-junction concentrator solar cells on Ge substrates”. In: *AIP Conference Proceedings*. Vol. 1766. 1. AIP Publishing, 2016, p. 080003. DOI: 10.1063/1.4962101.
- [17] John F. Geisz, Iván García, William E. McMahon, Myles A. Steiner, Mario Ochoa, Ryan M. France, Aron Habte, and Daniel J. Friedman. “Energy yield determination of concentrator solar cells using laboratory measurements”. In: *11th International Conference on Concentrator Photovoltaic Systems: CPV-11*. Vol. 1679. AIP Publishing, Sept. 2015, p. 040005. DOI: 10.1063/1.4931516.
- [18] E Yaccuzzi, E Barrigon, S Rodriguez, M Ochoa, Marcela Barrera, P Espinet-Gonzalez, J Garcia, M L Ibarra, H. Socolovsky, M D Perez, P Giudici, M. Alurralde, C Algora, Ignacio Rey-Stolle, and Juan Plá. “In-Situ and Ex-Situ characterization of III-V semiconductor materials and solar cells upon 10 MeV proton irradiation”. In: *28th European Photovoltaic Solar Energy Conference and Exhibition* (2013), pp. 526–530.
- [19] P. Espinet-González, E. Barrigón, M. Ochoa, L. Barrutia, V. Orlando, I. Rey-Stolle, and C. Algora. “Structural challenges in multijunction solar cells for ultra-high CPV”. In: *27th European Photovoltaic Solar Energy Conference and Exhibition* (2012), pp. 146–149.

Patent Application

- [20] C. Algora, L. Barrutia, I. Rey-Stolle, and M. Ochoa. *Célula solar multiunión de semiconductores III-V que contiene grafeno y método de obtención*. Patent application P201731223. 2017.

Other contributions

- [21] Pilar Espinet-González, Enrique Barrigón, Elisa García, Mario Ochoa, Laura Barrutia, Vincenzo Orlando, Pengyun Huo, Jesús Bautista, Iván García, Neftalí Núñez, M. Vázquez, and Ignacio Rey-Stolle y Carlos Algora. “Temas de Física Concentración fotovoltaica”. In: *Revista Española de Física* 27.2 (2013), pp. 27–29.