UNIVERSIDAD POLITÉCNICA DE MADRID

**ESCUELA TÉCNICA SUPERIOR
DE INGENIEROS DE TELECOMUNICACIÓN**

**OPTIMIZATION PATHWAYS TO IMPROVE GaInP/GaInAs/Ge
TRIPLE JUNCTION SOLAR CELLS FOR CPV APPLICATIONS**

TESIS DOCTORAL

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Licenciada en Ciencias Físicas
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Instituto de Energía Solar

Departamento de Electrónica Física

Escuela Técnica Superior de Ingenieros de Telecomunicación

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A la memoria de mi abuela Ole,
por todo el cariño y esfuerzo que siempre puso en nosotras.

A mi familia, a Andrés,
por todo su amor y apoyo constante.

*“Hay una fuerza motriz más poderosa que el vapor,
la electricidad y la energía atómica: la voluntad”*

Albert Einstein

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Resumen

La tecnología de concentración fotovoltaica (en inglés, *Concentration Photovoltaics*, CPV) ha experimentado un intenso desarrollo desde principios de los años 2000. En particular, las células solares de triple unión (GaInP/GaInAs/Ge) ajustadas en red siguen dominando el mercado CPV. Esta tesis pretende contribuir en la investigación de este tipo de célula multiunión desarrollada previamente en el *Grupo de Semiconductores III-V* del Instituto de Energía Solar de la Universidad Politécnica de Madrid (IES-UPM). Los distintos aspectos abordados para la mejora de la eficiencia de esta estructura comienzan desde el sustrato de Ge, que sustenta el resto de la estructura semiconductor, pasando por distintos aspectos de optimización de la estructura semiconductor, hasta la incorporación de grafeno como electrodo transparente en la parte superior del dispositivo.

Como primer punto, se aborda el crecimiento epitaxial de semiconductores III-V sobre sustratos de Ge. El estudio de la contaminación por Ge en las distintas capas semiconductoras es de especial interés, ya que una elevada concentración no intencionada de este material en las capas activas afecta negativamente a sus propiedades. En este estudio se presta especial atención tanto a la incorporación de Ge por difusión en fase sólida en las primeras capas semiconductoras crecidas, como a su incorporación desde la fase gaseosa durante el crecimiento mediante la epitaxia en fase vapor a partir de precursores metalorgánicos (en inglés, *Metalorganic Vapour Phase Epitaxy*, MOVPE) de las distintas capas. Para ello, se analiza la influencia de distintas condiciones y parámetros de crecimiento para encontrar el mejor proceso epitaxial para mitigar este efecto.

Continuando con el análisis de mejora del dispositivo, hemos abordado los tres aspectos más destacados que hemos detectado para la mejora de la célula solar de triple unión. En primer lugar, con motivo de la carga térmica acumulada y soportada por la subcélula de germanio durante el crecimiento del resto de la estructura, la V_{OC} resultante de ésta es menor de lo esperado. Con la intención de disminuir dicha carga térmica y mejorar la V_{OC} de la subcélula de germanio, hemos optimizado el proceso de nucleación. En particular, en esta tesis se presenta una nueva rutina de nucleación de la capa de nucleación de GaInP y de la capa buffer de GaInAs poniendo especial

interés en la reducción de la carga térmica como consecuencia de disminuir el espesor de estas capas, además de la bajada en temperatura a la que se crece la buffer de GaInAs.

El siguiente aspecto a analizar es la mejora de la subcélula de GaInP. Continuando con el uso de Sb como elemento surfactante durante el crecimiento de la base del GaInP, en esta tesis hemos desordenado aún más el GaInP con el uso de dicho surfactante tanto en el crecimiento epitaxial de la base como del emisor, con el objetivo de aumentar la banda de energía prohibida (band gap) de esta subcélula y por tanto su V_{OC} . En paralelo, hemos realizado la optimización la capa ventana de AlInP modificando ligeramente su contenido en aluminio y aumentando su dopado con el objetivo de minimizar la absorción de luz en dicha capa.

Por otro lado, con motivo de la integración de una nueva unión túnel entre la subcélula de GaInP y la subcélula de GaInAs, hemos detectado una resistencia serie elevada a altas concentraciones luminosas. Ya que esta unión túnel presentaba unas excelentes propiedades optoelectrónicas antes de integrarse en la célula solar, la resistencia serie elevada sugiere una mala heterounión entre las capas vecinas (especialmente de la capa ventana de la subcélula de GaInAs) y esta nueva unión túnel. Con el objetivo de reducir dicha resistencia hemos analizado distintos niveles de dopaje e incluso el uso de otros materiales en la capa ventana.

El desarrollo de estas mejoras se completa con su integración en célula completa de triple unión con el objetivo de estudiar su impacto final. La mejor célula de triple unión desarrollada previamente en el grupo se usa como referencia epitaxial (capas, dopados, etc). A esta estructura se van incorporando gradualmente las diversas mejoras produciendo diversas generaciones de dispositivos que son analizados y comparados mediante diversas técnicas de caracterización (curvas I-V, eficiencia cuántica, etc) con la célula de referencia. Como resultado de esta integración se han logrado eficiencias superiores al 40%. No obstante, se podrían haber logrado mayores eficiencias si todas las mejoras parciales hubieran sumado todo su potencial teórico. Se presenta un análisis de pérdidas para apuntar las causas de esta integración no óptima.

Como último aspecto desarrollado a lo largo de esta tesis doctoral, hemos abordado el estudio del potencial del grafeno para su integración en una estructura fotovoltaica multiunión de semiconductores III-V. El principal objetivo de la integración de este novedoso material es la mejora de extracción de corriente del dispositivo trabajando a altas concentraciones (disminución de la resistencia serie y, por tanto, mejora del factor de forma). Primeramente, hemos caracterizado sus propiedades tanto ópticas como eléctricas que nos permitan una implementación adecuada en una célula multiunión. Posteriormente, hemos realizado la transferencia e integración de grafeno en una célula de triple unión así como su análisis y comparación respecto al mismo

tipo de célula sin grafeno. Uno de los resultados de este trabajo ha sido una solicitud de patente sobre células solares multiunión de semiconductores III-V que incorporen grafeno.

Abstract

Concentration Photovoltaic (CPV) technology has been growing up intensively since the early 2000s. In particular, GaInP/GaInAs/Ge lattice matched triple junction solar cells are still dominating the CPV market. This thesis has focused on the investigation of this kind of multijunction solar cells aiming at further developing the basic technology previously developed in the *III-V Semiconductor Group* at the Solar Energy Institute of the Technical University of Madrid (IES-UPM). The different aspects that have been tackled in order to enhance the efficiency of this structure begin with the Ge substrate, which supports the rest of the structure, up to the incorporation of graphene on top of the device to serve as a transparent electrode.

Firstly, the epitaxial growth of III-V materials on Ge substrates is considered. Ge contamination along the semiconductor layers is of special interest, since the non-intentional incorporation of Ge in the active layers will have a detrimental effect on their properties. In this study, attention has been paid not only to the Ge solid-state diffusion that takes place at the first epitaxial layers next to the III-V/Ge heterointerface, but also to the incorporation of Ge from the gas phase during the epitaxial growth by Metalorganic Vapor Phase Epitaxy (MOVPE). Thus, the influence of different conditions and growth parameters are analyzed with the purpose of finding the best combination of process parameters to mitigate this effect.

Following with the device optimization, three main aspects detected as possible improvement mechanisms had been addressed. On the one hand, the V_{OC} of the Ge bottom cell is lower than expected, due to the accumulated thermal load of the growth of the rest of the MJSC structure. With the aim of mitigating such thermal load and improving this V_{OC} , several III-V on Ge nucleation strategies are studied. In particular, this Thesis presents a new nucleation routine of the GaInP nucleation layer and the GaInAs buffer layer where special attention has been paid to minimize their contribution to the thermal load in terms of thickness (i.e. growth time) and temperature.

The following step is the optimization of the GaInP subcell. Ensuing with the use of Sb as surfactant during the growth of the GaInP base, in this Thesis the GaInP subcell is further

disordered (i.e. its energy band gap is increased) with the use of Sb in both the base and emitter. The goal of this step is to increase the energy band gap of the GaInP subcell and thus its V_{OC} . Additionally, the AlInP window is optimized by modifying its Al composition as well as increasing its doping level with the aim of minimizing the light absorption in this layer.

In past works, we developed highly transparent high bandgap GaInP/AlGaAs tunnel junctions (TJ) with excellent performance as isolated devices. However, when such tunnel junctions were integrated between the GaInP and GaInAs subcells in complete triple-junction solar cells, we detected the presence of a non-negligible series resistance. In this thesis, we have analyzed this integration problem and found that it might be related to the heterojunction between the new TJ and the adjacent layers (specially, the window layer of the GaInAs subcell). With the aim of decreasing such series resistance, different doping levels as well as the use of other materials at this window layer were studied and the integration problem has been sorted out.

The implementation on a complete TJSC of these partial developments are consequently undertaken in order to evaluate their joint final impact. The best TJSC structure previously developed in our group is used as a reference and several new designs gradually introducing the partial improvements studied are analyzed and compared by different characterization techniques (I-V curves, external quantum efficiency...). The outcome of this integration has been the achievement of solar cell efficiencies in excess of 40%. However, higher efficiencies would have been reached if all the individual improvements had added their full potential. A loss analysis is presented to figure out the cause behind this non-optimum integration.

As the last part of this Thesis, the potential of graphene for its integration in a multijunction solar cell is considered. The main objective behind the use of this new material is to enhance the photocurrent extraction of the device when working at very high concentration levels (by reducing the lateral series resistance and consequently improving the fill factor). Several analyses on its optical and electrical properties are presented in order to allow for an adequate implementation in a multijunction solar cell. Finally, graphene layers are transferred and integrated in a multijunction solar cell and the performance of the resulting devices is compared with similar devices without graphene. As a result of this work, a patent on III-V semiconductor multijunction solar cells incorporating graphene has been filed.

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List of acronyms

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AFM	Atomic Force Microscopy
AM1.5D	Direct irradiance terrestrial reference spectrum
APBs	Antiphase Boundaries
APDs	Antiphase Domains
ARC	Anti-Reflection Coating
ARXPS	Angle Resolved X-ray Photoelectron Spectroscopy
BC	Bottom Cell
BLG	Graphene Bilayer
BSF	Back Surface Field
CB	Conduction Band
CCD	Charge-coupled device
CMOS	Complementary Metal-Oxide-Semiconductor
CPP	Clean Power Plan
CPV	Concentrator Photovoltaics
CVD	Chemical Vapor Deposition
DF	Dark Field
DJSC	Dual-junction Solar Cell
DNI	Direct Normal Irradiation
DOS	Density of States
DUT	Device under test
ECV	Electrochemical Capacitance Voltage
EL	Electroluminescence
EMA	Effective Medium Approximation
EQE	External Quantum Efficiency

FIB	Focused Ion Beam
FLG	Few Layers Graphene
FWHM	Full Width at Half Maximum
HAADF	High Angle Annular Dark Field Imaging
HVPE	Hydride Vapor Phase Epitaxy
IES	Solar Energy Institute
IMM	Inverted Metamorphic
IPA	Isopropanol
ITO	Indium Tin Oxide
I-V	Current-Voltage
J-V	Current density-Voltage
LCOE	Levelized Cost of Electricity
LEDs	Light-Emitting Diodes
LENS	Laboratory of Electron Nanoscopies
LOI	Layer of Interest
LPE	Liquid Phase Epitaxy
MC	Middle Cell
MIT	Massachusetts Institute of Technology
MJSC	Multijunction Solar Cell
MLG	Graphene monolayer
MOVPE	Metalorganic Vapor Phase Epitaxy
PCB	Printed Circuit Board
PL	Photoluminescence
PMMA	Polymethyl Methacrylate
ppm	Parts per million
PV	Photovoltaics
PVA	Poly(vinyl alcohol)
R2R	Roll to Roll
RAS	Reflectance Anisotropy Spectroscopy
RIE	Reactive Ion Etching
RF	Radio Frequency
rpm	Revolutions per minute
RT	Room Temperature

RTA	Rapid Thermal Annealing
SAED	Selected Area Electron Diffraction
SC	Semiconductor
sccm	Standard Cubic Centimeters per minute
SCR	Space Charge Region
SE	Spectroscopy Ellipsometry
SEA	Semilab Ellipsometric Analysis
SEL	Stop etching layer
SIMS	Secondary Ion Mass Spectroscopy
SLG	Single Layer Graphene
SMR	Spectral Matching Ratio
STEM	Scanning Transmission Electron Microscopy
TC	Top Cell
TCF	Transparent Conductive Films
TEM	Scanning Transmission Electron Microscopy
TJ	Tunnel Junction
TJSC	Triple junction Solar Cell
TLM	Transmission line method
TMAH	Tetra-methyl ammonium hydroxide
TO	Thin Oxide
UMM	Upright Metamorphic
UPS	Ultra Violet Photoemission Spectroscopy
UV	Ultra Violet (light)
UVL	Ultra Violet lithography
VB	Valence Band
VdP	Van der Pauw
vdW	Van der Waals

List of symbols

α	Fine structure constant
η	Efficiency
η	Order parameter
$\hbar$	Planck constant
θ_{APB}	Antiphase Boundary Angle
κ	Extinction coefficient
μ	Mobility
ρ_{FC}	Specific front contact resistance
Φ_b	Schottky barrier height
Φ_G	Graphene's work function
χ_e	Electron affinity
χ_{SC}	Semiconductor electron affinity
χ_{AlInP}	AlInP electron affinity
$\times$	Concentration (suns)
A_c	Solar cell Area
B	Magnetic Field
$CM_{\text{middle}}^{\text{top}}$	Current-matching (ratio) top middle
d	TLM pad length
e	Elementary electron charge
$E(\lambda)$	Spectral Irradiance
E_F	Energy of the Fermi level
E_g	Energy bandgap
FF	Fill Factor
FS	Shadowing factor
G_r	Growth rate
$I_{2D/1G}$	Intensity ratio between 2D and 1G Raman peaks of graphene
I_{SC}	Short-circuit current

J_{SC}	Short circuit current density
J_{01}	Saturation current density in the neutral region
J_{02}	Saturation current density in the depletion region
L	Diffusion Length
L_T	Transfer Length
ℓ	Distance between TLM pads
n_s	Sheet density of graphene
N_A, N_D	Dopant concentration for acceptors and donors, respectively
n	Refractive index
P_{in}	Input Power
$R_{E \text{ top Sheet}}$	Top emitter sheet resistance
R_e	Emitter sheet resistance
R_c	Metal Contact resistance of a TLM pad
R_g	Graphene sheet resistance
R_m	Sheet resistance of the front metal contact
R_{g-w}	Contact resistance between graphene-window layer
R_{g-m}	Contact resistance between graphene-metal
R_{SH}	Sheet resistance
$R(\lambda)$	Spectral Reflectance
r_s	Equivalent resistance
SRV	Surface recombination velocity
T	Temperature
$T(\lambda)$	Spectral transmittance
V_H	Hall Voltage
V_g	Gate voltage
V_{OC}	Open-circuit voltage
W	TLM pad with

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Chapter 1

INTRODUCTION

1.1. Introduction

The global energy landscape is affected by many factors such as economy prospects, policy and technology. In addition, population and demographics are important underlying determinants of energy use. The world population is expected to grow by 0.9% per year on average, from 7.3 billion in 2014 to 9.2 billion in 2040¹. With all these trends, energy consumption will increase significantly over the 28-year period from 2012 to 2040. The total world energy consumption was 437EJ² in 2001, 579EJ in 2012 and is expected to be 859EJ in 2040, this is a 48% increase from 2012 to 2040.

Additionally, the Paris Agreement on climate change entered into force in November 2016. With the goal of reducing global warming, the Clean Power Plan (CPP) requirement to reduce carbon dioxide emissions accelerates the shift towards less carbon-intensive generation (from fossil fuels to renewable energy).

¹ <https://www.iea.org/media/publications/weo/WEO2016Chapter1.pdf>

² 1 EJ = 277.7 TWh

In this respect, sunlight is considered as the most abundant energy resource in the planet. Taking into account scattered or absorbed solar flux by the atmosphere and clouds, the theoretical solar power potential at the Earth's surface is $\sim 89,300\text{TW}$ [Tsao et al. 2006]. This extractable potential overwhelmingly exceeds our energy demand. As an example, this theoretical potential represents more energy striking the earth's surface in one-and-a-half hours (480 EJ) than worldwide energy consumption in the year 2001 from all sources combined (430 EJ) [IEO 2005]. Additionally, harvesting solar energy for its subsequent conversion into electricity is not feasible at various regions of the Earth's surface such as oceans and very cold areas. By considering this, the extractable potential must be reduced by the fraction ~ 0.708 of the Earth's surface that is ocean and by the fraction ~ 0.0345 of the sunlight that is incident on freezing zones of the Earth [Tsao et al. 2006]. Anyhow, after these reductions, the solar power potential of $25,091.4\text{TW}$ is available, which still reinforces the exploitation of solar energy as an important renewable energy resource for electricity supply [Tsao et al. 2006].

Concentrator Photovoltaic (CPV) technology is based on Multijunction Solar Cells (MJSC) which are specially suitable for harvesting solar energy since they possess the highest conversion efficiency among PV technologies. The key principle of CPV is the use of cost-efficient optical components that concentrate the sunlight into a small area, allowing the use of more expensive and more efficient solar cells. MJSCs consist of multiple p-n junctions of III-V semiconductor materials following a tandem configuration, where each subcell is intended to absorb a portion of the solar spectrum and transform it into electricity. The subcells are arranged from the highest band gap to the lowest band gap to the path of light so photons with higher energies will be absorbed in the upper subcells and photons with lower energies will be absorbed in the lower subcells. With an infinite number of junctions, a theoretical efficiency of 86% might be achieved [Tobías et al. 2002].

In 2016, worldwide cumulative CPV installations reached 350MW [Wiesenfarth et al. 2017]. Even though CPV is at an early commercial stage, the current level of CPV costs has dropped and will continue in this way as long as the industry is scaled up by manufacturing [Haysom et al. 2015, Kurtz 2009]. CPV system prices, including installation, lie between 1 to $\text{€}3/\text{Wp}$ [Algora et al. 2016.] and 1.4 to $\text{€}2.2/\text{Wp}$ [Wiesenfarth et al. 2017] in comparison with PV technology which is $\sim \text{€}1/\text{Wp}$ [Taylor et al. 2015]. In addition, with a solar cell efficiency increase of 1% an average price reduction of CPV between $\text{€}0.043/\text{Wp}$ – $0.047\text{€}/\text{Wp}$ might be obtained [Algora et al. 2016., GTMResearch 2014]. Thus, several analyses agree in the potential of CPV to further reduce the levelized cost of energy (LCOE) if installations continue to grow and technological advances such as cell (with a record efficiency of 46%) and module efficiencies (with a record efficiency of 38.9% [van Riesen et al. 2015]) are obtained.

If installations continue to grow through 2030, CPV power plants at locations with a direct normal irradiation (DNI) of 2000 or 2500 kWh/m² per year could reach a cost ranging between €0.045/kWh and €0.075/kWh. System prices, including installation for CPV power plants would then be between €0.7/Wp and €1.1/Wp [Wiesenfarth et al. 2017]. This is consistent with the future CPV scenario presented by [Algora et al. 2016.], where a system price may be set equal to €0.95/Wp when a cumulative installed CPV of 1GWp is accomplished. All these forecasts reinforce the potential of CPV technology to catch up with regular flat-plate PV in several years.

The monolithic two-terminal lattice matched GaInP/GaInAs/Ge triple-junction solar cell is the established architecture that has been widely used in the CPV industry. This kind of solar cell has reached a record efficiency of 41.6% at 364× [King et al. 2009] and the state-of-the-art efficiency in industrial products is in the range of 39-41%. Additionally, new architectures are being developed such as 1) the upright metamorphic (UMM) [Guter et al. 2009]; 2) the inverted metamorphic (IMM)[Geisz et al. 2012, Sasaki et al. 2013]; 3) the wafer bonded design [Dimroth et al. 2016]; and 4) the lattice matched GaInP/GaAs/GaInNAs [Derkcas et al. 2012]. Some of these new technologies have already exceeded the efficiency of the lattice matched triple junction with champion efficiencies of 45.6% for 4J IMM [Green et al. 2015] and 46% for 4J wafer bonded [Dimroth et al. 2014]. In spite of this, the aforementioned lattice matched TJSC is still dominating the CPV market due to its robustness, technological maturity and lower price. That is why the main effort of this thesis has been to enhance even further the efficiency of the lattice GaInP/GaInAs/Ge triple junction solar cell developed at the Solar Energy Institute of UPM (IES-UPM). Although the analyses and developments of this thesis are focused on the TJSC, most of the outcomes of these Chapters could be also applicable to these new architectures.

1.2. State of the art: GaInP/GaInAs/Ge triple junction solar cell at IES-UPM

The III-V Semiconductor Group at IES-UPM has developed over the last years very high efficiency solar cells, with world records such as the GaAs solar cell with an efficiency of 26.2% at 1000 suns manufactured by Liquid Phase Epitaxy (LPE) [Algora et al. 2001]. With the acquisition of the first AIXTRON MOVPE reactor in 2001, another world record was achieved with dual junction solar cell (DJSC) with an efficiency of 32.6% from 499 up to 1020 suns [García et al. 2009]. Moreover, few years later, with the development of the lattice match GaInP/GaInAs/Ge TJSC, an efficiency of 39.2% at 400 suns was achieved in 2014 [Barrigón 2014].

By comparing this last TJSC architecture designed in our group with the world record efficiency of this kind of TJSC devices, which is 41.6% at 364 suns [King et al. 2009] it can be observed that is quite close and confirms the development at IES-UPM of a state-of-the-art technology for these devices.

A schematic of the lattice matched GaInP/GaInAs/Ge TJSC structure developed in our group is shown in *Figure 1.1*. A brief description (from the bottom to the upper layers) of the semiconductor structure is as follows:

- A single Ge substrate is used to grow all the materials for the three different subcells (Ge bottom cell (BC), Ga(In)As middle cell (MC) and GaInP top cell (TC)).
- All the semiconductors in this structure are lattice matched to the Ge substrate with a high material quality.
- The germanium wafer acts as both the bottom cell as well as a mechanical support of the complete MJSC stack.
- The BC is formed by diffusion of group-V elements in the p-type Ge wafer, during the growth of the GaInP nucleation layer.
- After the GaInP nucleation layer, a Ga(In)As buffer layer is grown to ensure a good quality template (good morphology) for subsequent growth.
- The three subcells are series-connected via tunnel junctions (TJ). A tunnel junction of $p^{++}\text{AlGaAs:C}/n^{++}\text{GaAs:Te}$ structure, sandwiched between AlGaAs barriers is used to connect the BC and MC. To connect the MC and TC, initially we used a $p^{++}\text{AlGaAs}/n^{++}\text{GaAs}$ TJ that was after superseded by a highly conductive and transparent $p^{++}\text{AlGaAs}/n^{++}\text{GaInP}$ TJ.
- A low Indium content (1%) is added in the Ga(In)As middle cell to match its lattice constant to the Ge substrate.
- The bandgap of the GaInP in the TC was varied with the use of Sb as surfactant during the growth of the GaInP base.
- A final GaAs cap layer was grown to ensure the formation of ohmic contacts.

TOP CELL	Contact	400nm, n ⁺ GaAs [Si,Te] $>2 \cdot 10^{18} \text{cm}^{-3}$
	Window	25nm, n ⁺ AlInP [Si] $>1 \cdot 10^{18} \text{cm}^{-3}$
	Emitter	175 nm, n ⁺ GaInP [Si] $\sim 7 \cdot 10^{17} \text{cm}^{-3}$
TUNNEL JUNCTION	Base	1300nm, p GaInP [Zn] $\sim 9 \cdot 10^{16} \text{cm}^{-3}$
	BSF	100nm, p AlGaInP [Zn] $\sim 4 \cdot 10^{18} \text{cm}^{-3}$
	Anode	25nm, p ⁺⁺ AlGaAs [C] $\sim 6 \cdot 10^{19} \text{cm}^{-3}$
MIDDLE CELL	Cathode	20nm, n ⁺⁺ GaInP [Te] $\sim 1 \cdot 10^{19} \text{cm}^{-3}$
	Window	20nm, n GaInP [Si] $1 \cdot 10^{18} \text{cm}^{-3}$
	Emitter	140nm, n GaIn _{0.01} As [Si] $\sim 6 \cdot 10^{17} \text{cm}^{-3}$
TUNNEL JUNCTION	Base	3000nm, p GaIn _{0.01} As [Zn] $\sim 1 \cdot 10^{17} \text{cm}^{-3}$
	BSF	150nm, p AlGaAs [C] $\sim 1 \cdot 10^{18} \text{cm}^{-3}$
	p-barrier	30nm, p AlGaAs [C] $\sim 5 \cdot 10^{19} \text{cm}^{-3}$
BOTTOM CELL	Anode	20nm, p ⁺⁺ AlGaAs [C] $\sim 5 \cdot 10^{19} \text{cm}^{-3}$
	Cathode	20nm, n ⁺⁺ GaAs [Te] $\sim 2 \cdot 10^{19} \text{cm}^{-3}$
	n-barrier	50nm, n ⁺⁺ AlGaAs [Te] $\sim 4 \cdot 10^{18} \text{cm}^{-3}$
	Buffer	1000nm, n GaIn _{0.01} As [Si] $\sim 1 \cdot 10^{18} \text{cm}^{-3}$
	Nucleation	375nm, n GaInP [Si] $\sim 1 \cdot 10^{18} \text{cm}^{-3}$
	Emitter	
	Base	
	Substrate p ⁺⁺ Ge	

Figure 1.1: Semiconductor structure of the GaInP/GaInAs/Ge solar cell developed at IES-UPM before this thesis with an efficiency of 39.2 % at 400 suns.

Regarding the processing of the TJSC structure, conventional photolithographic steps were used. Thermal evaporation of AuGe/Ni/Au for the n-type front contact was used as well as Au for the p-type back contact. The main front grid used in our III-V semiconductor group is the inverted square configuration which is designed to work at high concentration levels with an active area of 1mm² [Algora et al. 2000].

1.3. Goal of this Thesis

Even if the aforementioned TJSC presents a very high efficiency, during the development of such complex structure, different interesting aspects were found to hold potential for its further optimization. Accordingly, the goal of this thesis is to tackle such different points of the lattice matched GaInP/GaInAs/Ge triple junction solar cell to squeeze its efficiency even further. At the same time, new challenges such as the incorporation of graphene on the TJSC to reduce the series resistance at high concentration levels have been investigated for the first time.

In short, the challenges addressed in this Thesis are as follows:

Effect of Ge autodoping during III-V MOVPE growth on Ge substrates

The triple-junction solar cell (TJSC) structure studied and developed along this thesis consists of several III-V semiconductor layers grown on a Ge substrate. The crossed-diffusion that takes place during the epitaxial growth of III-V semiconductors on a Ge substrate must be understood and controlled. In addition to solid-phase diffusion, which is a phenomenon limited to the vicinity of the III-V/Ge interface, there is another source of Ge contamination than can affect all III-V layers throughout the growth, namely, Ge autodoping. Ge autodoping refers to the process by which Ge atoms leave the substrate, reach the gas phase and can be subsequently incorporated into the III-V epilayers during the MOVPE growth. Growth parameters such as temperature, V/III ratio, growth rate, as well as Ge wafer size and back side coating of the Ge wafer need to be studied to understand and mitigate as much as possible this Ge contamination that affects TJSC performance in a detrimental way.

Towards further development of the triple junction solar cell

Three main aspects of the triple junction solar cell have been identified to be potentially improved. On the one hand, the V_{OC} degradation that suffers the BC after the thermal load during the growth of the rest of the complete structure must be mitigated with new nucleation routines that focus on the reduction of both growth time and temperature. In this line, the V_{OC} of the Ge bottom cell will be studied in terms of capacitance voltage and SIMS profiles in order to understand the diffusion of group III and V elements, which are dopants in Ge. This is of key relevance when the Ge wafer also acts as a solar cell (as it is the case in the state-of-the-art GaInP/Ga(In)As/Ge triple junction solar cells) since the diffusion of these elements determines the configuration of the resulting Ge p/n junction and thus rules the solar cell performance. All these aspects need to be analyzed to find the adequate alternatives to reduce such degradation.

Secondly, the GaInP bandgap increase described at the reference TJSC developed in our group [Barrigón 2014], confirms that the use of Sb as surfactant during the epitaxial growth of the Zn-doped GaInP base of the TC was able to decrease the degree of order in the GaInP (increase the band gap). Since the TC emitter has shown also some degree of order in the group III sublattice, the use of Sb surfactant to grow a completely disordered Si-doped GaInP emitter should be faced, accordingly. Additionally, the minimization of the light absorption at the AlInP window can be optimized by modifying the amount of Al composition as well as the increase of its doping level.

Despite the fact that a highly transparent tunnel junction (TJ) was developed in the past, it has been demonstrated that its integration in TJSCs leads to an increase in the series resistance. This

might be indicative of a problematic hetero-interface between this TJ and the neighboring layers. Special attention needs to be paid to these interfaces.

Development and characterization of the improved triple-junction solar cell

As the different parts of the TJSC are optimized and developed along this thesis (Ge V_{OC} , high bandgap tunnel junction, high bandgap top cell...), they must be carefully added to the final TJSC semiconductor structure. Thus, the pertinent characterization of each design to evaluate such benefits needs to be accomplished. Moreover, the direct comparison with the reference lattice matched GaInP/GaInAs/Ge solar cell will be very helpful.

Electro-optical properties of graphene for photovoltaic applications

2D materials will have a revolutionary impact in the near future in many optoelectronic devices. In relation to this, one of the main challenges of this thesis is the study of the potential of graphene to enhance the efficiency of a MJSC by its incorporation as a transparent electrode. Prior to the integration of graphene on a TJSC device, a deep characterization of its electrical and optical properties for its application in photovoltaics and, in particular, in the field of MJSC working at high concentrations ($\sim 1000\times$) should be evaluated. The pertinent characterization as well as the transfer of graphene to a substrate of interest must be studied.

Integration of graphene on III-V concentrator solar cells

Graphene integration on concentrator MJSC architectures –and particularly on lattice matched GaInP/Ga(In)As/Ge triple junction solar cell– is a challenging task that must be also accomplished to confirm the potential of graphene on these kind of devices. Again, a deep characterization of these solar cells, where 1-2 monolayers of CVD graphene are incorporated, should be carried out.

1.4. Organization of this thesis

This thesis has been divided into 6 chapters in addition to the present Introduction, which is itself Chapter 1.

Chapter 2 deals with the undesired Ge incorporation that is present when III-V semiconductor layers are grown on a Ge substrate by MOVPE. Since Ge is found to be a dopant on these layers,

both solid-phase diffusion and gas phase autodoping will be evaluated in order to find the best growth parameters to mitigate this effect in our TJSC structures.

In Chapter 3, three main aspects related to the optimization of the high efficiency lattice matched GaInP/GaInAs/Ge TJSC developed in our group have been tackled: 1) Ge V_{oc} optimization; 2) additional GaInP disordering with the use of Sb as surfactant during both base and emitter epitaxial growth of the TC and optimization of the AlInP window layer in terms of Al composition and doping level; 3) mitigation of the series resistance detected once the high band gap tunnel junction has been incorporated in the complete TJSC.

In Chapter 4, some sets of TJSCs incorporating the main improvements detailed in Chapter 3 are analyzed and characterized by I-V curves, external quantum efficiency and concentration measurements. Comparison between these new designs and the reference TJSC previously developed in our group will be shown.

Chapters 5 and 6 are devoted to graphene as a novel material to integrate in a MJSC and in particularly into a TJSC. A key of the work was learnt and performed during 3.5 month long PhD candidate internship at MIT (April-July 2015) in the group led by Prof. Tomás Palacios. Chapter 5 is related to the study of few graphene monolayers grown by Chemical Vapor Deposition (CVD). The electro-optical characterization as well as the transfer to the desired substrate are some important aspects considered along the chapter. Chapter 6 is related to the incorporation of graphene into a TJSC structure. Comparison between TJSC without graphene and TJSC with one and two graphene monolayers are analyzed.

Finally, Chapter 7 presents a summary of the main aspects and results obtained during this research as well as future experiments that are ongoing or will be faced in a near future.

Chapter 2

EFFECT OF Ge AUTODOPING DURING III-V MOVPE GROWTH ON Ge SUBSTRATES

2.1. Introduction

As already described in the general introduction of this document, the triple-junction solar cell (TJSC) structure studied and developed along this thesis consists of several III-V semiconductor layers grown on a Ge substrate. Germanium wafers are heavily used in MOVPE as the substrate of choice for triple junction solar cells for space and terrestrial concentrator applications and some LEDs. Germanium has a lattice constant quite close to that of GaAs and offers some advantages over GaAs substrates such as lower cost, higher mechanical strength, virtually zero etch pit density and a slightly higher thermal conductivity. In the particular field of multijunction solar cells, which represents in excess of 80% of the world market for Ge substrates, Germanium has shown to be an excellent material to be used as the bottom cell (BC) [Friedman 2010]. This is because of Ge shows an adequate energy bandgap ($E_g \sim 0.66\text{eV}$), it can be employed as mechanical support of the stack and it enables the subsequent growth of a vast family of III-V materials (i.e., other subcells can be grown on top).

In relation to the use of Ge as the substrate for III-V based multijunction solar cells (MJSC), there are extra challenges regarding the epitaxial growth, in comparison to MJSC grown on GaAs or InP substrates. First, since Ge presents a non-polar structure, a heteroepitaxial routine is required to grow defect-free polar III-V layers on a Ge substrate. This can be accomplished by the use of a misoriented Ge substrate [Kroemer 1987], together with a dedicated surface preparation prior to growth [Barrigón et al. 2013, Barrigón et al. 2011, Brückner et al. 2012, McMahon et al. 2001]. Secondly, the crossed-diffusion that takes place during the epitaxial growth must be controlled. On the one hand, group III and V elements are dopants in Ge. This is of key relevance when the Ge wafer is intended to act as a solar cell (as is the case of GaInP/Ga(In)As/Ge triple junction solar cells) since the diffusion of these elements determines the configuration of the resulting Ge p/n junction and thus rules the solar cell performance [Andreev et al. 2004, Friedman et al. 2001]. On the other hand, Ge is in turn a dopant in III-V semiconductors as reported in several studies [Lee et al. 1993, Welser et al. 2008, Yoon et al. 2001], that can diffuse into the III-V epilayers during the epitaxial growth. We will refer to this process as *solid-phase* Ge diffusion.

In this scenario, where a wide range of III-V materials need to be grown on Ge to form complex solar cell or LED structures, it is of utmost importance to understand the impact of growing on Ge and the impact of the Ge autodoping on the active layers, other than the slight change in lattice constant as compared with GaAs. In addition to solid-phase diffusion, which is a phenomenon limited to the vicinity of the III-V/Ge interface, there is another source of Ge contamination that can affect all III-V layers throughout the growth, namely, Ge autodoping. Ge autodoping refers to the process by which Ge atoms leave the substrate, reach the gas-phase and can be subsequently incorporated into the III-V epilayers during the MOVPE growth (see *Figure 2.1*).

Figure 2.1: Sketch of the semiconductor structure of the first layers that form the BC of a MJSC. In these layers both Ge solid-phase diffusion (black arrows) and Ge gas-phase autodoping (blue arrows) take place due to the growth of III-V semiconductors on a Ge substrate by MOVPE. For the sake of clarity, we just represented the first layers of a complete MJSC, but it is important to remark that the impact of Ge gas-phase autodoping could be present during the whole growth of the MJSC not described in the figure.

Accordingly, Ge autodoping can be *direct* when it originates from Ge atoms that either evaporate from the substrate or are chemically etched away from the rear side of the wafer by H_2 [Oh et al. 2004], AsH_3 or PH_3 flows [McMahon et al. 2001]. Last but not least, Ge autodoping can be *indirect* when it stems from Ge atoms that are re-evaporated from the chamber walls due to reactor history. Even though special MOVPE routines have been developed to control the solid-phase diffusion of group-III and V elements on Ge and vice versa for III-V based MJSC [Bosi et al. 2011, Chia et al. 2008, Galiana et al. 2008], little attention has been paid to the Ge autodoping effect by gas-phase transport in a MOVPE ambient [Tobin et al. 1988, Wu et al. 2016].

Without the knowledge of this aforementioned effect, time consuming epitaxial growths and calibrations in our group were required in order to obtain the desired properties of the semiconductor layers in terms of intentional doping (i.e., p-type GaInP base doped with Zn). In many occasions, the optimized parameters were not optimum anymore after several growths, or from one size wafer to another (i.e., from 2-inch Ge wafer to 4-inch Ge wafer). All these aspects, encouraged us to have a better control of this Ge autodoping which is necessary to be understood in order to get rid out of time consuming calibrations and to achieve more solid and reproducible process (which is a very important aspect at the industry level).

With this goal, the work presented in this Chapter is divided into two main sections. Initially, some experiments were made in order to confirm the typical Ge diffusion profile that takes place in the first layers of our TJSC. The evolution of this diffusion profile due to the thermal load associated with the growth of a complete TJSC was also analyzed. The minimum thickness of the first two layers in the solar cell structure to contain such solid-phase diffusion so that it does not reach the active layers was also found. Secondly, a comprehensive study of the aforementioned Ge gas-phase autodoping was carried out. In particular, we studied two III-V materials, namely, $Ga_{0.99}In_{0.01}As$ (hereinafter noted as Ga(In)As) and $Ga_{0.51}In_{0.49}P$ (herein after simply noted as GaInP), which are the most intensively used in state-of-the-art triple junction solar cells and in particular in our triple junction solar cell (TJSC).

2.2. Ge solid-phase diffusion

2.2.1. Introduction

Ga(In)As and GaInP can be considered as the most commonly used materials for active layers of a subcell in a complete multijunction solar cell device. Different technology challenges appear

when growing either Ga(In)As or GaInP on Ge such as antiphase domains (APDs), misfit dislocations, Ge out diffusion, or Ga, In and As interdiffusion. Accordingly, different optimization processes have been studied along the last years at IES-UPM to tackle those challenges [Barrigón 2014, Galiana 2006, García 2010].

The negative effect that Ge solid-phase diffusion could have on the final performance of the TJSC could be mitigated as long as the Ge does not reach the active layers. Different techniques have been investigated during the last decades to decrease and stop at some point the cross diffusion that takes place between GaAs and Ge respectively. One of these methods consists in the growth of a thin AlAs layer that acts as a barrier blocking this cross diffusion. This effect was attributed to a higher Al-As bonding energy [Chia et al. 2008]. The disadvantage of this process is the high oxygen incorporation in Al-containing alloys that could lead to highly resistive layers. Another solution developed in the past in our group at IES-UPM was the growth of a thin GaAs nucleation layer at low temperature that acts as a barrier for Ge [Galiana et al. 2008]. Anyhow, we must comment that all these experiments were devised for GaAs nucleation layers grown on a Ge substrate.

However, when GaAs is used as the nucleation layer (first layer grown on top of the Ge wafer), as a result of the high diffusion coefficient of arsenic in Ge, very deep diffusion profiles are obtained which is a disadvantage for the specific requirements of the emitter of the Ge BC (as will be explained in Chapter 3). As an alternative, P-based materials, and in this case GaInP, have a lower diffusion coefficient in Ge ($D_P < D_{As}$) and thus provide shallower emitters and higher V_{OCs} in the bottom subcell. Therefore, the use of GaInP instead of GaAs as a nucleation layer presents some advantages to obtain a better performance of the bottom Ge subcell [Barrigón 2014].

2.2.2. Ge solid-phase diffusion in short processes with low thermal load

As it will be discussed in Chapter 3, in order to reduce the thermal load that suffers the bottom cell (BC) because of the growth of the rest of the layers that form the whole MJSC, it is desirable to reduce the thickness of some of the layers. At the same time, most of the active layers have been carefully optimized along previous work in our group [Barrigón 2014, García 2010] and minimal changes could imply critical consequences on the final device performance. Only some of the layers, such as the GaInP nucleation and the Ga(In)As overbuffer (see *Figure 2.1*), offer the possibility to further reduce them. With the aim of studying the impact of this thickness reduction on the Ge solid-phase diffusion, some experiments were performed. In order to simplify

the presentation of the results, *Table 2.1*, summarizes the growth parameters of three illustrative samples (A, B, C) analyzed for this purpose.

Table 2.1: Brief description of the parameters explored in this study for the growth of the GaInP nucleation and Ga(In)As overbuffer layers in three different variants, A, B and C.

	Sample	A	B	C
Bake	$T(^{\circ}\text{C})$	640	—	640
	Time(s)	600	—	600
Pre-nucleation	$T(^{\circ}\text{C})$	675	685	685
	Time(s)	60	60	60
GaInP nucleation	$T(^{\circ}\text{C})$	675	685	685
	Thicknes (nm)	350	350	150
	V/III ratio	414	414	420
GaInAs overbuffer	$T(^{\circ}\text{C})$	675	685	685
	Thicknes (nm)	1000	1000	250
	V/III ratio	8	8	8

For this study we followed our standard strategy for Ge substrate surface preparation with the help of in-situ monitoring using Reflectance Anisotropy Spectroscopy (RAS) [Barrigón et al. 2011]. Trimethylgallium (TMGa), Trimethylindium (TMIn) were used as the group III precursors, and PH_3 and AsH_3 as the group V precursors.

Due to morphological aspects of the GaInP nucleation layer, the nominal growth temperatures used for the GaInP were 675°C (A) and 685°C (B and C). This narrow range has proven to produce the minimum amount of defects (hillocks) in our reactor. The target thickness were 350 (A and B) and 150nm (C). To be able to compare the three samples already described in *Table 2.1*, they were grown using the same precursors, V/III ratios (~ 400 for the GaInP layers and ~ 10 for the Ga(In)As) and growth rates (0.21nm/s for the GaInP and 0.83nm/s for the Ga(In)As).

The growth temperature is the main factor that affects Ge solid-phase diffusion. With this in mind, the temperature at the wafer surface was recorded by a pyrometer (with an EpiTT tool from Laytec) during the growth. As shown by *Figure 2.2* and in agreement with the differences in nominal temperature, samples B and C were grown under the same temperature, while sample A, as expected, was grown a few degrees lower.

Figure 2.2: Temperature measured by in-situ pyrometry during the epitaxial growth of the GaInP nucleation layer for each sample (A, B, C).

To quantify the Ge incorporation in each layer of interest, Secondary Ion Mass spectroscopy (SIMS) was chosen as the primary diagnostic tool for these experiments since it is a very sensitive technique used to detect a vast variety of elements³. Additionally, Electrochemical Capacitance Voltage (ECV) profiling was also measured in our lab. However, in this chapter, we will be focused on SIMS analysis which reveals the chemical composition.

SIMS profiles are presented in Figure 2.3. Similar SIMS profiles have been reported in the literature when growing GaAs on Ge substrates at 650°C by Hydride Vapor Phase Epitaxy (HVPE) or GaInP on Ge substrates at 630°C by MOVPE [Schulte et al. 2013, Wu et al. 2016].

For an easier understanding, the description of the SIMS profile is performed for sample A (Figure 2.3 a). Looking at the first region of the SIMS profile (1), it corresponds to the Ge substrate since it is a flat region with Ge concentration in the order of 10^{22} at/cm³. Please note that the Ge concentration obtained here is slightly lower than the atomic density of a Ge crystal, which is 4.4×10^{22} at/cm³. This difference is attributed to the SIMS calibration procedure, which was

³ SIMS measurements were performed in an external company

optimized to obtain more accurate results in the rest of the regions where significantly lower concentrations are expected.

Both regions 2 and 3 correspond to the solid-phase diffusion and thus exhibit the typical kink-and-tail profile. Region 2 is the kink of the profile and can be defined as a sharp transition that has been found to vary between 35-50nm [Schulte et al. 2013, Wu et al. 2016]. In our case it ranges from ~40-50 nm in agreement with the data in the literature. The diffusion mechanisms that govern this region are not well understood yet. It seems that several mechanisms are involved in the diffusion of Ge into the GaInP and vice-versa [Wu et al. 2016]. Even if the main diffusion mechanism is vacancy-mediated [Schulte et al. 2013], other factors such as Ge segregation at the initial growth could have a significant effect as presented by [Grützmacher et al. 1993]. Region 3 corresponds to the tail part of the diffusion profile of Ge, which has been discussed to be quite similar to that of Si. The profile obtained at this region has been explained by pair diffusion [Greiner et al. 1984] and vacancy dependence [Kavanagh et al. 1987] when GaAs was grown on a Ge substrate. Not too many works have been found in relation to the mechanism that explains the Ge diffusion when a GaInP layer is grown on it. Wu et al also considered a di-vacancy diffusion model to explain not only the Ge diffusion mechanism but also the ordering effect in the GaInP layer [Wu et al. 2016]. This Ge out-diffusion increases the density of di-vacancy and enhances the inter-diffusion of the host atoms.

Finally, regions 4, and 5 are attributed to Ge gas-phase autodoping of the GaInP and the Ga(In)As layers, respectively, defined as regions with a flat Ge concentration.

Looking at the SIMS profiles for sample A (*Figure 2.3 a*) and B (*Figure 2.3 b*), it can be observed how the depth of the Ge solid-phase diffusion into the GaInP layer is around ~168 nm for a nucleation temperature of 685°C and slightly thinner ~163nm when the nominal temperature is decreased to 675°C. Moreover, the presence of a bake prior to nucleation in samples A and C (10 min long, performed with PH₃ at 640°C) seems to not affect the solid-phase diffusion profile. This is in consistence with previous studies performed by [Barrigón 2014] where, from the point of view of the emitter formation of the BC, this bake was shown not to have a direct influence either in the doping level of the emitter or in its thickness. The Ge bottom cell (BC) will be further commented in Chapter 3.

Figure 2.3: SIMS measurements of samples A (a); B (b) and (c)

For samples A and B, with GaInP nucleation layers of 350nm, which is the standard value that has been used during the development of the TJSC at IES-UPM, it can be observed that after the first 170nm, the Ge concentration becomes constant at $1 \cdot 10^{18}$ at/cm³. This indicates that at this point Ge gas-phase autodoping starts to be the dominant doping mechanism. Additionally, the Ga(In)As overbuffer that is actually grown after the GaInP nucleation layer, also could help to prevent Ge solid-phase diffusion reaching the active layers. This is not the main role of this Ga(In)As layer which is mainly grown to improve the morphology and prepare the best surface in terms of smoothness for the growth of the rest of the semiconductor layers with the best crystalline quality. Anyhow, as it can be observed, the Ge gas-phase autodoping is further reduced (down to the SIMS detection limit for these experiments) when the Ga(In)As layer is grown because of the growth conditions, as will be discussed in the next section. Please note that despite 1000nm of Ga(In)As were grown in both samples (A, B), just the first ~ 500nm are shown in order to simplify the figures.

Finally, looking at the SIMS profile of sample C (where a thinner 150 nm GaInP layer was grown), we can observe how the Ge solid-phase diffusion has penetrated across the nucleation layer. This is in fact expected, since the penetration depth of this Ge solid-phase diffusion is in the order of ~170 nm for this growth conditions. Additionally, Ge incorporation is drastically reduced when the Ga(In)As starts to be grown at the same temperature (in this case 685°C) which reinforces the idea of using this layer as a barrier to stop Ge solid-phase diffusion coming from the GaInP nucleation layer. As it occurred on sample B, at this point Ge gas-phase autodoping becomes the dominant doping mechanism.

2.2.3. Ge solid-phase diffusion in TJSC processes with high thermal load

It is important to recall that the SIMS profiles already described for samples A, B and C do not correspond to a complete TJSC. In the real case of a solar cell, the thermal load originated during the growth of the rest of the semiconductor layers would have a detrimental effect on these results yielding a deeper Ge solid-phase diffusion profile. In order to verify this effect, another similar experiment was performed. Furthermore, with the aim of reducing such thermal load and of studying which are the thickness limitations of both GaInP and Ga(In)As layers, a thinner GaInP nucleation layer of just ~50 nm was developed during the growth of a complete TJSC. The description of the pre-nucleation routine together with the parameters used during the growth of both nucleation and overbuffer layers are briefly presented in *Table 2.2*.

Table 2.2: Brief summary description of the pre-nucleation, nucleation and overbuffer routine for the growth of the two first layers of a TJSC growth by MOVPE and analyzed by SIMS.

	Sample	TJSC
Bake	$T(^{\circ}\text{C})$	640
	Time(s)	10
Pre-nucleation	$T(^{\circ}\text{C})$	675
	Time(s)	60
GaInP nucleation	$T(^{\circ}\text{C})$	675
	Thickness (nm)	50
	V/III ratio	430
Ga(In)As overbuffer	$T(^{\circ}\text{C})$	600
	Thickness (nm)	500
	V/III ratio	8

As it can be observed, the main changes (in bold font) are the reduction of the nucleation layer thickness (down to $\sim 50\text{nm}$), together with the reduction of the Ga(In)As thickness (down to $\sim 500\text{nm}$) and its nominal growth temperature down to 600°C .

Figure 2.4: SIMS measurement of 50nm GaInP nucleation layer (nominal temperature of 675°C) and 500nm Ga(In)As overbuffer layer (nominal temperature of 600°C) of a complete MJSC structure grown on a Ge (100) substrate.

The Ge concentration as measured by SIMS in this structure can be seen in Figure 2.4. The additional thermal load associated with the growth of the whole TJSC structure is behind the evolution of the Ge solid-phase diffusion profile, as compared with the profiles in Figure 2.3. In

Figure 2.4, we find a much higher Ge concentration in the Ga(In)As and a much deeper penetration of the Ge solid-phase diffusion ($\sim 265\text{nm}$ in total, resulting from 50nm of GaInP and $\sim 215\text{ nm}$ of Ga(In)As).

Additionally, Figure 2.5 shows that the temperature measured by pyrometry was virtually the same for the GaInP nucleation growth of both TJSC and samples B and C of Figure 2.2. Given this fact and the fact that the overbuffer layer is grown at a significantly lower temperature of 600°C , we can conclude that the differences in the profiles in Figure 2.4 and Figure 2.3 are mostly affected by the thermal load of the growth of a full TJSC.

Figure 2.5: In situ temperature measured by pyrometry during the epitaxial growth of the GaInP nucleation layer of a complete TJSC together with sample (A, B, C). According to this figure, the temperature recorded for the TJSC nucleation layer was in the range of the temperatures obtained for samples A, B and C.

This Ge solid-phase diffusion could be interpreted as a Ge semi-infinite source that is affected by both growing temperature and time. Indeed, it can be observed that the Ge solid-phase diffusion penetrates into the Ga(In)As layer (see the “jump” indicating the GaInP/Ga(In)As interface) up to 215nm . With this experiment several conclusions can be extracted. On the one hand, it seems that the critical GaInP thickness measured before by SIMS ($\sim 168\text{nm}$) to stop the solid-phase diffusion is not acceptable when a complete TJSC is to be grown. If a thin GaInP nucleation layer ($\sim 50\text{ nm}$) wants to be developed, the Ga(In)As overbuffer that is grown after the GaInP nucleation layer should be thick enough to effectively act as a barrier to contain the Ge diffusion profile, so it does not reach active adjacent layers such as tunnel junctions. Moreover, the Ga(In)As thickness (for these growing conditions) could be reduced down to 230nm from the 1000nm of the initial design, since 215nm have been shown to be thick enough to withhold such

Ge solid-phase diffusion in the critical case of growing a very thin GaInP nucleation layer (~50nm).

It has been mentioned before that, when GaAs was used as a nucleation layer on Ge substrates, several strategies were developed in order to hinder or minimize Ge solid-phase diffusion. The most successful among those strategies consisted in the use as nucleation layer of a thin GaAs layer grown at low temperature ~ 475°C, prior to the growth of 1000nm of GaAs at 625°C, which acted as the buffer [Galiana 2006]. Without that GaAs barrier grown at low temperature, the Ge solid-phase diffusion penetrated 800nm into the GaAs layer. However, with this new approach the penetration was reduced to 100nm. It is worth to mention that neither these experiments suffered the thermal load present in our TJSC, so these values should change in a detrimental way as it has been shown. Accordingly, and looking at the results of the SIMS profile presented in *Figure 2.4*, it is clear that using a thin GaInP layer of ~50nm before the Ga(In)As greatly decreases this Ge penetration depth, as compared to the low-temperature GaAs case. In addition, the growth of this first thin GaInP layer is performed without decreasing the growth temperature, and with high quality crystal growth and with smooth surfaces. Consequently, what it is also presented with the SIMS results of *Figure 2.4* is an alternative way to reduce the Ge solid-phase diffusion that is always present in any optoelectronic device when a Ga(In)As layer needs to be grown on a Ge substrate without the requirement of reducing the temperature.

2.2.4. Influence of Si₃N₄ as a backside coatings

The MOVPE reactor that was acquired by our group at IES-UPM in 2001, was a horizontal AIX200 reactor with the capacity of a single 2-inch wafer per run. Four years later, in 2005 the capacity of the reactor was upgraded to handle 4-inch wafers too (AIX/200-4).

The development of the TJSC has been basically done on 2-inch Ge wafers along this thesis. At the same time, with the opportunity of growing in 4-inch Ge wafers, some of the experiments concerning this Chapter were also performed on 4-inch substrates. Thus, to finish this Ge solid-phase diffusion section, we wanted to present the SIMS profiles measured for two kinds of 4 inch-Ge wafers. The main difference between them –that will be further described in the following section 2.3– is the use of a backside coating of Si₃N₄ (thickness ~100nm). The characteristics of the epitaxial structure used to perform these experiments is described in more detail in section 2.3.3 (see *Figure 2.9*).

Figure 2.6: a) SIMS measurement of 350 nm GaInP nucleation layer (620°C) and 300nm Ga(In)As overbuffer layer (620 °C) on a Ge (100) substrate with (black dots) and without Si₃N₄ backside coating layer (green dots). b) Sketch of the Ge atoms autodoping mechanisms for a Ge substrate with (at the top) and without a backside coating of Si₃N₄ (at the bottom).

Figure 2.6.a plots the Ge concentration of the first two layers (GaInP and Ga(In)As) in both samples as measured by SIMS. On the one hand, no significant change is observed at the Ga(In)As layer, where similar Ge concentration is detected in both samples. On the other hand, looking at the GaInP layer, in the curve for the uncoated sample (green dots), we can clearly identify both the Ge solid-phase diffusion and gas-phase autodoping regions. On the contrary, in the curve for the Si₃N₄ coated sample (black dots) a deeper solid-phase diffusion profile can be identified, with no clear trace of the gas-phase autodoping region. Our hypothesis for the explanation for this behavior is visually described in Figure 2.6 b. On the one hand, without a backside coating layer, Ge atoms in the bulk of the wafer feel two driving forces, one towards the front surface to feed the diffusion into the III-V layers and one towards the back surface to compensate for the injection of vacancies that results from Ge escaping to the gas-phase. On the other hand, depositing a backside coating layer reduces the injection of vacancies at the back and thus, increases the net driving force of the Ge atoms to diffuse across the GaInP/Ge interface enhancing the solid-phase diffusion mechanism. Along the next section, we will describe how important is the presence of this backside coating layer to reduce the amount of Ge concentration that comes from the gas-phase, especially for bigger wafers such as 4-inch. Additionally, in coated wafers, the mechanical stress in the crystal lattice might be different from wafers without such coating. Accordingly, this might result in an influence and in a difference on the diffusion mechanism taking place from one kind of wafer to another. As it has been mentioned, the speculations made from our preliminary results need to be refined with future experiments.

To conclude this study, a GaInP thickness of $\sim 300\text{nm}$ would have been enough to stop Ge solid state diffusion for a 4-inch Ge wafer but not for a 4-inch Ge wafer covered with a back coating of Si_3N_4 , where a thicker thickness of more than 350nm will be needed. For the Ga(In)As overbuffer, it can be observed in both wafers that its thickness can be further reduced from the nominal 300nm down to 120nm approximately. One more time, a pertinent calibration of these layers needs to be considered when growing a complete MJSC.

As a summary from the first section of this Chapter, Ge solid-phase diffusion had been evaluated. SIMS measurements were carried out in order to find the minimum thickness of the first two layers (GaInP nucleation and Ga(In)As overbuffer) grown in our TJSC to withhold this Ge solid state diffusion so it does not reach the active layers. At the most critical situation where just 50 nm of GaInP were grown as a nucleation layer, the following Ga(In)As buffer layer of 215nm was found to be thick enough to stop such diffusion. At the same time, this thin GaInP layer could be also used as an alternative way to mitigate the Ge solid-phase diffusion penetration that is always present in any optoelectronic device when a Ga(In)As layer needs to be grown on a Ge substrate. Additionally, the solid-phase diffusion profile as the result of using a Si_3N_4 coating wafer was also evaluated resulting in a deeper solid-phase diffusion profile.

2.3. Ge gas-phase autodoping

2.3.1. Introduction

This section of the chapter is focused on the study of the Ge gas-phase autodoping, which is present during the whole growth of our TJSC structures. As revealed by several of the SIMS profiles discussed in the last section, Ge gas-phase autodoping produced a significant contamination in GaInP layers in many samples. In order to understand this phenomenon and to better control this effect a wide set of experiments have been carried out.

Firstly, GaInP solar cell structures have been grown under different reactor conditions to illustrate the impact of Ge gas-phase autodoping on the device performance. Secondly, to understand and control this effect, a set of growth experiments have been designed for two of the main materials used in a TJSC, namely, Ga(In)As and GaInP. In these experiments we have studied: 1) influence of the V/III ratio; 2) influence of the growth rate; 3) reactor at different conditions (i.e. reactor history); 4) influence of temperature; 5) the use of 2-inch versus 4-inch Ge substrates and 6) the use of Ge substrates with Si_3N_4 backside coating.

2.3.2. Preliminary assessment of the effect of Ge autodoping in GaInP top cells

In order to have a preliminary idea of the importance of Ge autodoping in the characteristics of GaInP top cells (TC) we grew two GaInP /Ge dual junction solar cells (DJSC), namely, DJSC_1 and DJSC_2 in two different reactor pre-conditions, which are as follows:

- DJSC_1: reactor clean, ready to start a new batch of epitaxial growths with clean quartz elements such as the liner, as well as a clean graphite susceptor.
- DJSC_2: the reactor chamber and the different reactor elements are not clean since they have “seen” several III-V semiconductor epitaxies (of several microns).

In both cases the top GaInP cell was grown under the same process conditions, including the exact same nominal temperature of 675°C, which corresponded to a $T_{\text{pyrometry}} \sim 647.5^\circ\text{C}$. All in all, the key difference between the samples is the reactor coatings and history. Again, SIMS measurements were used to measure the concentration of Ge in the different layers of the structure.

Figure 2.7: SIMS measurements of two GaInP/Ge dual junction solar cells (DJSC_1 and DJSC_2) grown with two different reactor conditions. The growth parameters used for the nucleation and the buffer layer were already described in Section 2.2.2.

Figure 2.7 shows the Ge profiles, as measured by SIMS, of both DJSC_1 (black circles) and DJSC_2 (green circles). As Figure 2.7 makes evident, there are obvious differences in Ge concentration between both samples that affect both the GaInP nucleation layer as well as the GaInP TC. The Ge concentration obtained at the GaInP TC of DJSC_1 is almost one order of magnitude lower than that of DJSC_2. On the contrary, the Ge concentration obtained for the Ga(In)As buffer was quite lower and actually no difference can be observed between both samples. It should be recalled that the growth of the top cell in both cases is performed using the same growth parameters and hence such large differences are the result of uncontrolled processes associated with reactor history.

As it was already pointed out, a Multijunction Solar Cell Structure (MJSC) is a complex structure that consists of more than 20 layers of III-V ternaries and quaternaries of the arsenide and phosphide families. In order to achieve a good performance of the solar cell it is mandatory that each layer achieves specific characteristics in terms of thickness, doping level, etc. In particular, for the GaInP TC, its base should have low doping levels (around $0.8\text{-}1\cdot 10^{17}\text{ cm}^{-3}$) to have a good EQE response. This is because in state of the art n-on-p MJSC design, the photogeneration of carriers takes place mainly in the p-type base of the subcells. In essence, the doping level of this layer determines the minority carrier lifetime and in turn the external quantum efficiency (EQE). However, as it has been just shown in Figure 2.7, the presence of Ge autodoping creates a strong n-type background in GaInP layers which is going to make it very difficult to achieve a controllable p-type doping in the GaInP base in the ranges mentioned above ($\sim 10^{17}\text{ cm}^{-3}$). This is so because the net p-doping in the GaInP TC base will be the result of the compensation between Zn intentionally put (i.e., the DMZn molar flow) and the Ge autodoping effect. To illustrate this point, three new GaInP/Ge dual junction solar cells were grown again under the same process conditions (temperature, V/III ratio and growth rate). In this case, the three solar cells were grown in a row so reactor conditions should be similar and should not play a role. The key difference between samples was the amount of DMZn molar flow (mol/min) used in the p-type base of the GaInP subcell. In essence, we generated a sample with low DMZn, a sample with optimum DMZn and a sample above optimum DMZn and then the GaInP top cell performance was analyzed by EQE. Figure 2.8 a shows the EQE of the three GaInP TCs just described. Please note that no anti-reflection coating layer (ARC) was used on these samples. As it can be observed, if the DMZn employed is too low (blue curve in Figure 2.8 a), a minimum EQE is obtained. This response can be understood in the light of the ECV profile of this junction shown in Figure 2.8 b. In this particular case, the non-intentional Ge autodoping overrides the intentional Zn doping and the structure of the solar cell actually becomes a $n^+ \text{ GaInP} / n \text{ GaInP} / p^+ \text{ AlGaInP}$ heterojunction instead of the nominal $n^+ \text{ GaInP} / p \text{ GaInP} / p^+ \text{ AlGaInP}$. Therefore, the amount of DMZn injected in the reactor chamber should be increased in order to compensate for

Ge autodoping. This is in turn what happens in the magenta curve in *Figure 2.8 a* where DMZn flow was optimized to compensate Ge and achieve the desired p-type $\sim 10^{17} \text{ cm}^{-3}$ doping in the base. Finally, if DMZn flow is increased too much (black curve in *Figure 2.8 a*), then minority carrier lifetime in the p-GaInP base is deteriorated and EQE drops again.

Figure 2.8 a): EQE of GaInP solar cells grown on Ge substrates with different amount of DMZn molar flows. *b):* ECV profile indicating the presence of a n++GaInP/nGaInP region rather than a n GaInP-p GaInP junction as a result of Ge contamination.

Despite in this particular example a good EQE has been achieved by tweaking the DMZn flow, this is only practicable when Ge autodoping is low. In addition, the presence of Ge in the layers has been reported to produce deep levels that limit the collection efficiency of the cell [Gonzalez et al. 2011, Welser et al. 2008, Yang et al. 2011]. Therefore strategies to reduce the Ge autodoping effect would be desirable to enhance the photovoltaic properties of the GaInP layers.

All in all, Ge gas-phase autodoping has been shown to play an important role during the growth and optimization of GaInP solar cells. In our search to understand, control and minimize this effect, in the following sections we analyze the influence of several factors on this Ge gas-phase autodoping.

2.3.3. Influence of the growth rate and V/III ratio

In order to evaluate the influence of V/III ratio and growth rate on the incorporation of Ge for both GaInP and Ga(In)As layers, a set of experiments varying this parameters were performed.

Figure 2.9 shows the basic semiconductor structure employed for this study. It consists of a set of alternating GaInP and Ga(In)As layer pairs grown lattice matched to the Ge substrate. Growth parameters such as V/III ratio, temperature and growth rate used for each GaInP/Ga(In)As layer

pair will be indicated for each experiment. Layers were grown nominally undoped so any Ge content should come from either solid-phase diffusion or autodoping.

Figure 2.9: Schematic of the structures grown for this study based on alternating GaInP/Ga(In)As epilayers grown on Ge for SIMS analysis. Depending on the experiment, different temperatures have been used for the different pairs of layers. Details of the temperatures used (T_1 , T_2 and T_3) will be indicated when discussing each experiment.

To account for possible run-to-run temperature variations, the wafer surface temperature was monitored in-situ using pyrometry. Along this section we will include both the nominal target temperature for each experiment (T_{nominal}), which corresponds to the reading of the thermocouple embedded in the susceptor holding the wafer, as well as the value obtained by pyrometry ($T_{\text{pyrometry}}$). The quantification of the Ge atoms being incorporated along the layers was once more determined by SIMS measurements. In most cases, a layer thickness of $\sim 300\text{nm}$ was grown. In some runs, thinner layers of around 100 nm were used for the Ga(In)As. Anyhow, in all cases it was checked that layers were thick enough as to obtain a plateau free of boundary effects where the intensity of the autodoping could be assessed. Moreover, Ge concentration in each layer is calculated as the average of the concentrations obtained from the SIMS measurements only at the central part of each layer. Correspondingly, the uncertainty in the concentration value has been assumed to be equal to the standard deviation.

Figure 2.10: SIMS results of the Ge concentration (at/cm³) incorporated in both Ga(In)As and GaInP layers as function of the (a) V/III ratio for a constant growth rate of ~0.23 nm/s and (b) growth rate (G_r) for a constant V/III ratio of 46 for the GaInP and 33 for the Ga(In)As. The extension of the error bars accounts for the standard deviation of the mean value.

For this first batch of experiments, alternating GaInP and GaInAs layers were grown lattice matched on 2-inch Ge substrates and the growth temperature was set to a nominal value of 675°C (T_{pyrometry} 620°C) for all the layers (T₁=T₂=T₃). To vary the V/III ratio, the partial pressure of the group V precursor was varied –PH₃ in the case of GaInP and AsH₃ in the case of Ga(In)As– while the partial pressures of the group III precursors were kept constant to yield a growth rate of 0.23nm/s. Three pairs of GaInP/Ga(In)As layers were grown, with increasing V/III ratios for each

pair. *Figure 2.10 a* represents the evolution of Ge concentration in Ga(In)As (green squares) and GaInP (blue circles) as a function of V/III ratio. This figure essentially shows that the higher the V/III ratio the higher the Ge concentration. In addition, Ge incorporation is higher for Ga(In)As than for GaInP layers (a factor 2 and 3 for V/III ratios of ~ 65 and ~ 130 , respectively). The mechanism behind this difference could be the faster Ge wafer etching when AsH_3 is used instead of PH_3 [McMahon et al. 2001, Olson et al. 1998]. This different etching rate provides a higher partial pressure of Ge during the growth of Ga(In)As layers which results in a higher Ge incorporation in these layers.

Finally, in order to discard the possibility that the results of *Figure 2.10.a*) were affected by the order in which layers were grown (i.e. steady increase of V/III ratios) an additional set of samples was grown in which the structure of *Figure 2.9* was capped with a final pair of GaInP/GaInAs layers repeating the same conditions as in the first pair (low V/III ~ 65). The corresponding SIMS analyses (not shown here) have provided essentially the same Ge incorporation (considering the measurement uncertainties), ruling out any significant influence from the order in which the experiments were performed. In addition, we included a couple of control samples with repeated experiments grown in different order to check the run-to-run reproducibility, which was again confirmed to be within the uncertainty of the SIMS measurements.

A similar procedure was followed to assess the influence of the growth rate. For this purpose, the partial pressures of the group-III precursors were increased for each pair of layers achieving growth rates of around 0.2, 0.5 to 0.9 nm/s in the different pairs. To maintain the V/III ratio constant (at values of 46 for GaInP and 33 for Ga(In)As), the partial pressure of group-V precursor was varied accordingly. *Figure 2.10.b* shows the evolution of the Ge concentration in Ga(In)As and GaInP as a function of the growth rate. As it can be observed, as the growth rate increases the Ge concentration remains almost constant or even decreases slightly. However, this cannot be fully clarified as a result of the uncertainty in the measurements. Anyhow, what is evident is that the effect of the growth rate (while keeping the V/III ratio constant) on Ge autodoping is not as strong as the V/III ratio influence. This behavior can be explained considering the fact that the incorporation of the dopants is proportional to the dopant partial pressure and inversely proportional to the partial pressure of the species competing for a site in the same sublattice [Kurtz et al. 1992]. Since Ge has been found to be an n-type dopant for both GaInP and Ga(In)As, its incorporation competes with that of group-III elements (Ga and In). In addition, as it was already mentioned, in order to maintain a constant V/III ratio in this experiment, the group-V partial pressure was scaled as much as those of group-III to reach a certain growth rate. Therefore, as growth rate is increased so is group-V partial pressure and thus the release of Ge atoms from the back of the substrate as a result of etching. However, this increase in Ge availability is

counterbalanced by a proportional increase of group-III atoms competing for the same sublattice sites. The effects, of these competing phenomena, appear to cancel out and almost no impact of the growth rate on the Ge concentration at a constant V/III ratio is observed in *Figure 2.10 b*.

Finally, it should be noted that we do not observe any deposit on the rear side of the Ge substrate either when growing GaInP or Ga(In)As. In this respect, we can consider that the rear side of the substrate is acting as a semi-infinite source of Ge atoms and therefore, no depletion of Ge should occur along the epitaxial process.

In the light of these results, we can now better understand why the Ge incorporation was systematically higher in the GaInP layers analyzed in former sections as compared to Ga(In)As layers (*Figure 2.3* and *Figure 2.4*). We typically use much higher V/III ratios to grow GaInP than to grow Ga(In)As layers and, as *Figure 2.10 a*) shows, the high V/III is a booster for efficient Ge incorporation. These growth conditions were chosen since they allow us to obtain layers with minimum roughness and minimum defect density in our horizontal flow MOVPE reactor. Therefore, these conditions are necessary to maintain good morphologies along the growth of very complex structures (such as our multijunction solar cells) but, as demonstrated in this section, do not necessarily lead to the minimization of Ge autodoping effects (particularly in the case of GaInP).

2.3.4. Influence of the growth temperature and reactor preconditioning

As we have discussed above, the etching of the Ge substrate by the hydrides involved in the MOVPE process is key for Ge autodoping. Growth temperature may increase the etching rate, which will in turn enhance Ge autodoping. Despite the MOVPE reactor has never been used to grow Ge, the reactor pre-conditioning (reactor history, preexisting reactor coatings...) might play an important role in gettering some Ge. The influence of the reactor preconditions on the Ge incorporation was already observed in *Figure 2.7*. Since etching will mostly occur at the perimeter and the backside of the Ge substrate, the ability of etched Ge atoms to reach the growing surface will strongly depend on what environment they encounter in their trip to the front side (coatings on the substrate and /or the substrate susceptor, substrate size, etc). In order to shed some light on these effects, a study of Ge autodoping was done for three different reactor conditions at three different growth temperatures for both GaInP and Ga(In)As layers without any intentional doping. In this section, for each reactor pre-condition (to be described later) each pair of GaInP and Ga(In)As layers of *Figure 2.9* were grown at different temperatures, namely starting with the higher temperatures and going down to minimize Ge solid-phase diffusion ($T_1=675^\circ\text{C}$, $T_2=600^\circ\text{C}$ and $T_3=550^\circ\text{C}$). In this experiment, GaInP and Ga(In)As were grown at growth rates of 0.21 and

0.65 nm/s and V/III ratios of 410 and 16, respectively, since those are the conditions of our baseline TJSC process.

The three different reactor pre-conditions used are briefly summarized in *Table 2.3*. With pre-condition #A, a GaAs coating was deposited on the chamber except for the recess in which the substrate sits during the growth (i.e. the backside of the Ge substrate is directly in contact with the graphite of the susceptor). In reactor pre-condition #B, the same coating was done but covering the whole chamber (i.e. the backside of the Ge substrate is directly in contact with the GaAs coating on the susceptor). Finally, in reactor pre-condition #C, a more complex coating consisting of GaAs (500nm) followed by thicker GaInP and GaAs layers ($\sim 1.5\mu\text{m}$ each) was done also on the whole chamber.

Table 2.3: Schematics of the three reactor pre-conditions used in the growths.

	#A	#B	#C
Reactor Pre-conditions
Coating	GaAs (1500 nm)	GaAs (1500 nm)	GaAs/GaInP/GaAs (500 nm/1500nm/1500nm)
Temperature used to grow the coating	675°C	675°C	675°C
Coated areas	reactor chamber walls + susceptor (except for the recess of the substrate)	reactor chamber walls + susceptor + satellite	reactor chamber walls + susceptor + satellite

In order to ensure a fair comparison between the results of the different coatings, the wafer surface temperature was measured in-situ with a pyrometer in each experiment and is plotted in *Figure 2.11*. As shown in this figure, three different temperatures steps can be identified as expected from the nominal temperatures set and each step was at the same temperature for the three growths, regardless of the reactor conditions used in each case.

Figure 2.11: Temperature measured by in-situ pyrometry during the epitaxial growth of the III-V layers for each reactor condition.

After the epitaxial growth, the samples were characterized by SIMS and the profiles obtained are shown in Figure 2.12 where a different color is used for each reactor condition (green, red and black). From the right to the left in Figure 2.12 (a), four regions can be observed, labeled 1 to 4. The SIMS profile observed is as the one described in section 2.2.2 at the beginning of this Chapter (Figure 2.3 a). The first region, labelled as (1), consists of an abrupt or steep interface of $\sim 25\text{nm}$ where the Ge concentration decreases to $5 \cdot 10^{18} \text{ cm}^{-3}$; region (2) follows and shows a more gradual tail-like profile, where Ge concentration decreases from $4 \cdot 10^{18}$ to $\sim 3 \cdot 10^{17} \text{ at/cm}^3$. Regions (1) and (2) constitute the expected kink and tail profile already described for the solid-phase diffusion of Ge from the substrate into the first-grown GaInP epilayer [Wu et al. 2016]. Region (3) is attributed to gas-phase autodoping, since the Ge concentration is relatively flat for all the three temperatures. Figure 2.12 b shows a zoom-in of the profiles associated with Ge autodoping for GaInP and Ga(In)As grown at 675°C , namely, region (3). For the case of reactor pre-condition #C (black line), where a thicker and more complex coating of GaAs/GaInP/GaAs was done prior to growth, it was found that the Ge concentration in the layers was a factor ~ 2.5 lower ($9.7 \cdot 10^{16} \text{ atoms/cm}^3$) than in the other two cases. At this point, it is difficult to ascribe the better performance of coating #C to the increase in thickness or to the presence a thick GaInP layer. Anyhow, we speculate that the reason for this reduction is that the thick GaAs and/or GaInP layers in the coating act as efficient gettering centers for part of the Ge atoms escaping from the substrate as well as block the escape of possible Ge contamination from the susceptor. For the two other

reactor pre-conditions #A and #B, the Ge concentration was not reduced significantly and it was virtually the same for both ($\sim 2.5 \cdot 10^{17}$ atoms/cm³). Regarding the Ga(In)As layer grown at 675°C, a lower Ge doping level than GaInP grown at the same T was achieved for the three different reactor pre-conditionings ($\sim 4 \cdot 10^{16}$ atoms/cm³ for reactor pre-conditions #C while $\sim 7 \cdot 10^{16}$ for the other two pre-conditions) which can be attributed to the lower V/III ratio used to grow the Ga(In)As, as shown in section 2.3.3. Following the SIMS analysis in *Figure 2.12*, it can be seen that Ge concentration further decreases when the temperature goes down from 675°C to 600°C and then to 550°C (region 4), reaching a value $\sim 4 \cdot 10^{16}$ atoms/cm³. However, although it has been demonstrated that lower temperatures help reduce the amount of Ge atoms that are incorporated via gas-phase transport [Oh et al. 2004], *Figure 2.12* shows the stagnant value of $4 \cdot 10^{16}$ atoms/cm³. This is because this level represents the SIMS detection limit for Ge in our measurement, so this value should be considered as an upper bound for Ge concentration in these layers and not an accurate determination of the real Ge concentration in them. Anyhow, background doping values in this range can be tolerated in solar cell applications.

Figure 2.12: a) Ge concentration quantified by SIMS in the III-V layers of the structure of *Figure 2.9*. For these particular experiments, the thickness of the Ga(In)As layers was reduced to ~ 100 nm (shaded blue areas). For each reactor pre-condition (A, B and C) the layers were grown at three different nominal temperatures of 675°C ($T_{\text{pyrometry}} \sim 620^\circ\text{C}$), 600°C ($T_{\text{pyrometry}} \sim 575^\circ\text{C}$) and 550°C ($T_{\text{pyrometry}} \sim 530^\circ\text{C}$). b) Magnification of the area shaded in gray (region 3) where the main influence of each reactor pre-condition is observed.

As a conclusion for this batch of experiments performed on 2-inch Ge substrates, the following can be stated: 1) different reactor pre-conditioning have an impact on Ge autodoping; in particular, susceptor coatings having double GaAs and GaInP layers show a clear gettering/blocking effect decreasing the incorporation of Ge into the epilayers; and 2) at growth temperatures lower than 600°C the Ge concentration is equal to or lower than our SIMS detection limit ($\sim 4 \cdot 10^{16}$ atoms/cm³) which is low enough for our target TJSC.

2.3.5. Impact of the Ge substrate size: 4-inch versus 2-inch.

In order to assess the influence of wafer size, similar experiments were performed on 4-inch Ge substrates. In this case, only reactor pre-condition #C was used (i.e. wafer backside in contact with a GaAs/GaInP coating on the graphite susceptor). The experiment consisted again in the growth of the structure depicted in *Figure 2.9* following the same recipe as for the 2-inch wafers discussed in the previous section, and ensuring that the wafer surface temperature was the same despite the change in wafer size.

Table 2.4: Ge average concentration values as measured by SIMS at the center of each wafer for GaInP and Ga(In)As layers grown on 2 and 4 –inch Ge substrates at a nominal temperature of 675°C. Growth conditions were as follows: 1) for GaInP; $G_r=0.21$ nm/s and $V/III > 400$; 2) for Ga(In)As; $G_r=0.65$ nm/s and $V/III=16$.

Layer	2-inch-Ge wafer	4-inch-Ge wafer
GaInP	$9.7 \cdot 10^{16} \pm 34\%$	$6.6 \cdot 10^{17} \pm 22\%$
Ga(In)As	$< 3 \cdot 10^{16} \pm 12\%$	$< 3 \cdot 10^{16} \pm 19\%$

One more time, SIMS measurements were performed in points at the center of each wafer. For this particular case, Ge autodoping comparison (between 4-inch and 2-inch wafers) is presented only for one of the GaInP and Ga(In)As pair of layers grown at 675°C (see *Table 2.4*). As this Table shows, when using 4-inch Ge substrates, no change is observed in Ge incorporation for Ga(In)As, which still remains at our lower detection limit. This is consistent with the low V/III ratio (~ 16) used to grow this layer. However, there is a significantly higher Ge concentration in GaInP –which is grown at a considerably higher V/III ratio (> 400)–, with an increase of a factor of ~ 6 as compared with the 2-inch substrates. This suggests that the availability of Ge atoms to contribute to autodoping is greatly affected by the increase in the substrate size, this being a strong proof that Ge autodoping is mainly an area driven phenomenon rather than a perimeter driven phenomenon. However, the increase in surface from 2-inch to 4-inch wafers only accounts for a factor of 4, whereas *Table 2.4* shows a 6-fold increase in Ge concentration. Accordingly, other factors should also play an influence. In this respect, we believe that the greater bowing that 4-inch wafers experiment –as compared with 2-inch– would allow a more efficient release of Ge atoms from the backside towards the growing surface at the front of the wafer. Also as a result of bowing, it is possible that the gettering effect of the susceptor coating on these larger wafers is less effective. However, the latter should be considered just a speculation since we did not reproduce this experiment with reactor pre-conditions A and B.

As a conclusion for this batch of experiments it can be stated that the Ge concentration resulting from gas-phase autodoping is perfectly tolerable in Ga(In)As for both wafer sizes. On the contrary, Ge concentration seems in the limit to be manageable in the case 2-inch wafers, whilst it is way too high in 4-inch for our target TJSC.

As the conditions we use to grow GaInP make it more sensitive to Ge autodoping, in the following sections we will focus just on GaInP.

2.3.6. Influence of a Si₃N₄ backside coating of the Ge substrate.

With the aim of reducing the high Ge autodoping effect found in GaInP layers grown on 4-inch substrates, Ge wafers with a 100nm thick Si₃N₄ coating layer on the backside were employed [Schulte et al. 2013]. Again, the same batch of experiments were performed on Ge substrates with and without Si₃N₄ followed by identical SIMS analysis at the center of the wafer. *Table 2.5* shows how this back coating layer reduces the amount of Ge atoms being evaporated/etched from the substrate and thus reduce the Ge concentration especially in the GaInP layers. As this table shows, for the highest temperatures of 700°C and 650°C, a reduction by a factor ~ 3 was obtained. Please note that for these particular experiments, a second batch of SIMS measurements was carried out for which the SIMS detection limit for the GaInP layers was reduced down to concentration levels of $1.5 \cdot 10^{16} \text{ cm}^{-3}$.

Table 2.5: Ge concentration from autodoping as measured by SIMS for GaInP epilayers grown at different nominal temperatures of 700°C ($T_{\text{pyrometry}} \sim 650^\circ\text{C}$), 650°C ($T_{\text{pyrometry}} \sim 610^\circ\text{C}$) and 615°C ($T_{\text{pyrometry}} \sim 585^\circ\text{C}$) on 4-inch Ge substrates with and without Si₃N₄ backside coating. Growth conditions were $G_r=0.21 \text{ nm/s}$ and $V/III > 400$.

<i>Growth Temperature</i>	<i>700°C</i>	<i>650°C</i>	<i>615°C</i>
<i>Ge concentration (cm⁻³) without Si₃N₄ coating</i>	$1.2 \cdot 10^{18} \pm 6\%$	$1.1 \cdot 10^{17} \pm 23\%$	$1.5 \cdot 10^{16} \pm 60\%$
<i>Ge concentration (cm⁻³) with Si₃N₄ coating</i>	$4.0 \cdot 10^{17} \pm 11\%$	$3.8 \cdot 10^{16} \pm 33\%$	$\leq 1.5 \cdot 10^{16} \pm 55\%$

As a conclusion for this batch of experiments it can be stated that when Si₃N₄ coatings are used the Ge concentration resulting from gas-phase autodoping lies again in the manageable zone for 4-inch wafers.

2.3.7. Difference between substrate center and perimeter.

To conclude this study, Ge SIMS profiles were measured at the center and at the edge of 4-inch Ge substrates (with and without Si₃N₄ back coatings) and results are shown in *Table 2.6*. As seen

in this table, Ge gas-phase autodoping is more severe at the edge than at the center for all temperatures and for both coated and bare wafers. This is so, even despite the fact that the edge of the epiwafer should be slightly cooler than the center –as a result of wafer bowing in 4-inch substrates–, because the edge of the epiwafer is exposed to larger quantities of evaporated Ge as it is closer to the rear side. Therefore, as germanium is mainly incorporated at the edge its concentration in the gas-phase radially decreases towards the center of the epiwafer. In Table 2.6, it can be also observed how the Si_3N_4 layer actually helps to reduce this Ge autodoping. For a growth temperature of 650°C on Si_3N_4 coated wafers, both the edge and the center of the wafer show Ge concentrations resulting from autodoping in the mid-range of 10^{16} cm^{-3} (a value which is acceptable for solar cell applications). Obviously, Ge autodoping increases notably with temperature and, at 700°C, values are unbearably high for both coated and uncoated wafers (especially at the perimeter). This can be explained by the fact that the number of Ge atoms evaporated and/or chemically etched at the back surface of the substrate will probably show an Arrhenius-like dependence with temperature, together with the assumption that bowing will increase with temperature thus allowing a more efficient transport of Ge atoms from the rear side of the substrate.

Table 2.6: Ge concentration from autodoping as measured by SIMS in GaInP layers at the center and at the perimeter of the epiwafer. The layers were grown at two different nominal temperatures of 700°C ($T_{\text{pyrometry}} \sim 650^\circ\text{C}$) and 650°C ($T_{\text{pyrometry}} \sim 610^\circ\text{C}$) on 4-inch Ge substrates with and without Si_3N_4 backside coating.

	Growth T (°C)	700°C	650°C
<i>Ge concentration (atoms/cm³) in wafers without Si₃N₄ coating</i>	<i>Center</i>	$1.2 \cdot 10^{18} \pm 6\%$	$1.1 \cdot 10^{17} \pm 23\%$
	<i>Perimeter</i>	$7.6 \cdot 10^{18} \pm 11\%$	$6.9 \cdot 10^{17} \pm 12\%$
<i>Ge concentration (atoms/cm³) in wafers with Si₃N₄ coating</i>	<i>Center</i>	$4.0 \cdot 10^{17} \pm 11\%$	$3.8 \cdot 10^{16} \pm 33\%$
	<i>Perimeter</i>	$2.0 \cdot 10^{18} \pm 5\%$	$6.4 \cdot 10^{16} \pm 37\%$

2.4. Summary and conclusions

In this Chapter, two Ge doping mechanisms (Ge solid-phase diffusion and Ge gas-phase autodoping) have been evaluated when growing III-V semiconductors on Ge substrates by MOVPE, as is the case of the lattice matched TJSC.

On the one hand, Ge solid-phase diffusion on III-V materials, especially on Ga(In)As layers, had been already studied in the past. The goal of the first part of this Chapter was to study the Ge solid-phase diffusion profile obtained for our particular TJSC design where a Ga(In)As nucleation layer had already been substituted by a GaInP one. As a consequence of the set of experiments performed it could be concluded that the Ge solid-phase diffusion is generally mitigated at the

GaInP nucleation layer. Only at the most critical situation where just 50 nm of GaInP were grown as a nucleation layer, the following Ga(In)As buffer layer of 215nm was found to be thick enough to stop such diffusion avoiding the Ge atoms from the solid-phase diffusion mechanism to reach into the active layers such as tunnel junctions. At the same time, this thin GaInP layer could be also used as an alternative way to mitigate the Ge solid-phase diffusion penetration that is always present in any optoelectronic device when a Ga(In)As layer needs to be grown on a Ge substrate. Additionally, the solid-phase diffusion profile as the result of using a Si_3N_4 coating wafer was also evaluated resulting in a deeper penetration.

On the other hand, Ge autodoping plays an important role when growing GaInP and Ga(In)As III-V semiconductors on Ge substrates by MOVPE. Growing parameters such as temperature and V/III ratio directly influence the incorporation of Ge into GaInP and Ga(In)As layers grown on Ge wafers. In general, higher temperatures and higher V/III ratios produce higher Ge incorporation levels while the growth rate (while keeping the V/III ratio constant) does not seem to have a major impact on Ge incorporation. Ga(In)As seems to be more affected than GaInP by Ge autodoping, which could be attributed to a higher partial pressure of Ge present in the gas-phase as a result of a more severe Ge substrate etching when AsH_3 is used (instead of PH_3) as the group-V precursor. Moreover, Ge autodoping is also affected by the MOVPE reactor preconditioning. In this sense, different coatings on the reaction chamber have been shown to have a large impact on Ge autodoping for 2-inch substrates and Ge incorporation can be minimized by coating the susceptor on which the wafer sits with Ga(In)As and GaInP layers to block and trap Ge atoms. In addition, the impact of both the substrate size and radial dependence of Ge doping concentration in the epiwafer has been analyzed. In this respect, Ge autodoping has been found to be more severe in larger wafers, suggesting that it is mainly an area-driven phenomenon. Finally, in all cases it has been shown that coating the backside of the Ge substrates with Si_3N_4 is an efficient way to minimize the effects of Ge autodoping for the range of growth temperatures explored in this work.

Chapter 3

TOWARDS FURTHER DEVELOPMENT OF THE TRIPLE-JUNCTION SOLAR CELL

3.1. Introduction

The GaInP/Ga(In)As/Ge triple junction solar cell developed in our group, has demonstrated to be a robust structure with a very high efficiency when working at high concentration levels. Additionally, as any optoelectronic device, optimization paths to enhance its efficiency have been assessed and will be presented along this chapter. As it was previously mentioned in the Introduction of this Thesis, we have dealt with different aspects of the aforementioned triple junction solar cell. The first section of this chapter will be focused on the optimization of the Ge bottom cell (BC). The following section will address the optimization of the GaInP top cell (TC), and the final section will tackle the series resistance observed due to the incorporation of the high band gap tunnel junction between the GaInP TC and the Ga(In)As MC. Simulations indicate that the efficiency of the TJSC could reach over 40% at 1000 suns, by following these avenues.

3.2. Optimization of the Ge bottom cell

3.2.1. Introduction

In triple-junction solar cells (TJSC), p-type Ge wafers are used as the *active* substrate of the whole structure, as they enable the formation of the Ge bottom cell (BC). The latter is carried out by the in-diffusion of group-V elements (which are n-type dopants in Ge) during the growth of the nucleation layer.

In standard TJSC designs, the Ge junction is series-connected with the Ga(In)As and GaInP subcells. The photocurrent produced by the whole device will be limited by the subcell producing the least current. However, the Ge BC is not likely to limit the overall short circuit current since it is highly overstimulated by the full infrared part of the solar spectrum, as compared with the other two subcells. Thus, the main contribution of a Ge BC junction is to add as much open-circuit voltage as possible, which is actually not very high for such a low bandgap material. Therefore, the study and optimization of the V_{OC} of the germanium BC will be presented below.

3.2.2. Bottom cell junction formation

It is well known that one of the most critical factors to optimize the open circuit voltage in the Ge BC is related to the emitter depth. Since diffusion of both group-III and group-V species dominates the emitter formation (as will be shown with SIMS measurements), this layer ends up highly doped and partially compensated, which leads to a reduced minority carrier lifetime. Subsequently, reverse saturation current is increased (due to higher recombination) and V_{OC} of the BC is decreased. Moreover, [Friedman et al. 2001] reported that in a Ge solar cell, with a base doping of $\sim 10^{18} \text{ cm}^{-3}$ the main influence of the open circuit voltage (V_{OC}) will not be only the emitter thickness but also other emitter properties such as doping level, diffusion length (L) and surface-recombination velocity ($SRV_{emitter}$). That is why we have paid special attention to understand in detail how BC emitter formation occurs.

A set of samples with a structure as described in *Figure 3.1.b* were grown to analyze the BC doping profile, which was in turn studied by electrochemical capacitance voltage (ECV) measurements (see an example in *Figure 3.1.a*). The emitter thickness has been taken to be equal to the depth of the first p-type point measured in the (ECV) profile. With ECV we are able to see the electrical doping emitter profile resulting after the diffusion of III-V elements into the Ge substrate and vice-versa (we have seen in Chapter 2 how Ge diffuses into the III-V layers).

To complete this study, additional SIMS measurements were conducted in order to shed some light on the multiple and simultaneous diffusion processes occurring in the Ge wafer and the subsequent compensation mechanisms taking place.

Figure 3.1 a) shows the characteristic BC emitter profile formed during the growth of the GaInP nucleation layer on top of the Ge substrate. As it was mentioned in Chapter 2, the use of a GaInP nucleation layer allows the formation of shallower emitter profiles [Barrigón 2014], as compared to the use of arsenides due to the lower diffusion coefficient of phosphorus in Ge [Dunlap 1954]. Looking at the ECV measurement from left to right, we can identify different regions. An n-type gradual region (blue squares) starts at the GaInP/Ge interface (marked with a black oval) which evolves to an almost flat plateau with a higher doping level. Then, the emitter profile starts to decrease again until it reaches the space charge region (SCR) associated with the n-p junction. The first p-type point is detected at a depth of $\sim 186\text{nm}$. Finally, the base region is an almost flat p-type doping (red squares) which corresponds to the doping of the Ge wafer. All the Ge wafers used in this study were identical and Ga doped $\sim 3 \cdot 10^{18} \text{ cm}^{-3}$.

Figure 3.1: a) ECV measurements of the typical doping profile in a Ge BC formed during the GaInP nucleation layer growth in our lab. SCR refers to the space-charge region formed at the junction interface. b) Sketch of a structure of the BC samples grown for this study that correspond to the two first layers grown in a TJSC. The GaInP nucleation layer is responsible of the BC emitter formation due to P diffusion.

In order to interpret the shape of this ECV profile, SIMS measurements were carried out. Looking at the SIMS profile (Figure 3.2), we can observe how P diffuses deeper into the substrate with the characteristic kink-and-tail profile [Kobeleva et al. 2013] being the main element responsible for the emitter formation (by compensation of the p-type dopant, i.e., Ga, of the substrate). P remains as the dominant element until it is compensated by Ga atoms at $\sim 186\text{nm}$ in depth. Accordingly, we can confirm that SIMS measurements are consistent with ECV (where an emitter depth of $\sim 186\text{nm}$ was also measured). Additionally, a shallower diffusion profile is

observed for Ga and In which is in agreement with their lower diffusion coefficients. Note how the Ga profile reaches a flat plateau that corresponds to the intentional p-type doping of the Ge substrate. Since In and Ga are p-type dopants in Ge, their shallow diffusion creates an additional p-type doping close to the heterointerface that partially compensates the n-type phosphorus profile. Ga and In compensation is not strong enough to revert to p-polarity and they simply reduce the net n-type doping, producing the gradual region detected at the beginning of the emitter in the ECV profile.

Figure 3.2: Ge, P, Ga and In SIMS profiles in our conventional Ge BC structure. Ga and P elements were quantified, whereas Ge and In were not fully quantified and are given in counts/second.

3.2.3. Mitigation of the thermal load during Ge bottom cell formation

3.2.3.1. Studies on Ge single cells

Previous studies in our group have confirmed that the V_{OC} obtained in Ge cells grown as single junction devices is significantly higher than that of a Ge BC in a TJSC. This degradation is the result of the extra thermal load suffered during the growth of the whole TJSC structure. As it was confirmed by SIMS measurements (not shown in this document), III-V elements diffuse further into the Ge wafer which results in a deeper emitter profile in both thickness and gradual region (being the latter less affected). Further experiments performed in our TJSCs reveal a drop in short-circuit current density in the BC of $\sim 2.3 \text{ mA/cm}^2$ (due to thicker emitters), as compared to

analogous devices grown as single junction Ge solar cells on same type of substrates [Barrigón et al. 2017]. Concerning V_{OC} , the loss can be as high as 55 mV, which is a dramatic number for a subcell that provides $V_{OC} \sim 250\text{mV}$ in champion devices. Last but not least, the surface recombination velocity at the GaInP/Ge interface will also have an effect on these results.

With the aim of minimizing the thermal load effects on the Ge BC, several changes in our nucleation routine were investigated. *Table 3.1* summarizes these new nucleation routines, which basically consist in the reduction of the thickness of both the GaInP nucleation layer and Ga(In)As buffer layer along with the reduction of the growth temperature for the Ga(In)As buffer. The thickness reduction is aimed at shortening the growth times and thus diminishing the thermal load. Other nucleation strategies were also studied (such as changing the surface preparation with PH_3 from the beginning of the growth or 1second prior to the GaInP nucleation growth; an increase in the bake time prior to the growth from 10 minutes to 20 minutes,...) but no significant change or even worse V_{OC} s were obtained.

Table 3.1: Summary of the main differences explored for three different samples regarding the growth of both the GaInP nucleation layer and the Ga(In)As buffer during the BC emitter formation.

Nucleation routine	GaInP nucleation		Ga(In)As buffer	
	Thickness and T	Growth time	Thickness and T	Growth time
A (Reference)	375nm at 675°C	26'45''	1000nm at 675°C	20'
B	50nm at 675°C	3'37''	500nm at 600°C	10'
C	50nm at 675°C	3'37''	50nm at 675°C	1'

Table 3.1 shows that in these two new nucleation routines (B and C) the GaInP nucleation layer thickness was set to a nominal value of $\sim 50\text{nm}$. This value was chosen since it has been reported that lower thickness (below 35nm) might allow the through-diffusion of arsenic into the Ge coming from Ga(In)As buffer layer [Stan et al. 2008]. If this were the case, the arsenic would partner with phosphorus in the BC emitter formation. In order to prevent this fact, the conventional GaInP nucleation routine together with the conventional Ga(In)As buffer layer of $\sim 1000\text{nm}$ will be used as reference (named nucleation A).

The differences in the emitter formation of these three nucleation routines can be appreciated in the ECV profile of *Figure 3.3*. On the one hand, as expected, shallower emitters can be achieved with both thickness and temperature reduction in the nucleation and buffer layers. On the other hand, the gradual region at the emitter surface has been slightly modified with a shallower profile.

Figure 3.3: ECV profile of the Ge BC formation for the different nucleation routines (A, B and C). Solid symbols are n type, whereas empty symbols are p type.

The differences in electrical performance of the three profiles were studied. Both dark I-V curves (Figure 3.4) and Internal Quantum Efficiency (IQE) (Figure 3.5) reveal a better performance for the two new nucleation routines.

Figure 3.4: Dark I-V curves of the three different BCs with nucleation profiles A, B and C.

From, the dark I-V curves, it can be clearly observed that a better performance is achieved when both nucleation routines B and C are employed. In particular, for nucleation B (red dots) a lower recombination current was achieved with respect to the conventional nucleation A. This better performance, will lead to a V_{OC} gain as will be shown in Table 3.2 and might be associated with the lower temperature used to grow the GaInAs buffer layer ($\sim 600^{\circ}\text{C}$) for this nucleation routine.

Regarding IQE from *Figure 3.5*, the first point to note is that the part corresponding to wavelengths below 700nm (shaded in gray) where big differences become evident should be ignored in our analysis. This is because to measure the IQE we etched away the GaInAs layer but the GaInP nucleation layer remained on the samples. As such GaInP layer has different thickness in each sample, the response in the range from 300 to the bandgap of GaInP (~ 685 nm) will be filtered differently in each structure. So in our analysis we will focus on the spectral range above 700nm, which is the part truly comparable. The main emitter contribution to the IQE it is between 700-1200nm, while the main base contribution is between 1200-1600nm. It can be observed that no major changes appear associated with the base region, which is actually expected since the Ge wafers used for each sample were nominally the same. On the contrary, some differences can be related to the different emitters, being nucleation B the one with the best response. This might be indicative of better minority carrier properties (lower degradation), that might stem from the thermal load reduction.

Figure 3.5: Internal quantum efficiency (IQE) of the BCs with nucleation routine A, B and C.

Finally, *Table 3.2* shows a summary of the photovoltaic parameters of the three nucleation strategies of *Table 3.1*. As shown in the table, V_{OC} in sample B is improved with a gain of $\sim 22\text{mV}$ regarding the standard nucleation A, whereas in the case of sample C that gain is of only $\sim 13\text{mV}$. Concerning J_{SC} , nucleations B and C produce very similar increases of $\sim 2.5\text{mA}/\text{cm}^2$.

Table 3.2: Summary of the J_{SC} and V_{OC} values for the different Ge BC nucleation routines

<i>Nucleation routine</i>	<i>GaInP nucleation</i>	<i>Ga(In)As buffer</i>	$J_{SC} (\text{mA}/\text{cm}^2)$	$V_{OC} (\text{mV})$
A (Reference)	375nm at 675°C	1000nm at 675°C	19.8	249
B	50nm at 675°C	500nm at 600°C	22.3	271
C	50nm at 675°C	50nm at 675°C	22.2	262

The results just illustrate how important is the role of the thermal load, as the best performance was achieved for the nucleation routine B where the Ga(In)As buffer layer was grown at a lower temperature (600°C). Thus, future works will focus on the reduction of the GaInP nucleation temperature down to 600°C in order to further improve V_{OC} . This is in fact not an easy task since lower temperatures typically lead to a deterioration of the roughness and morphology of GaInP layers [Barrigón 2014].

3.2.3.2. Integration of the Ge BCs in TJSC structures

To understand the real impact of these optimizations of single Ge solar cells on complete devices, TJSC structures were grown integrating the aforementioned nucleations A, B and C of *Table 3.2*. Subsequently, the GaInP TC, Ga(In)As MC, and tunnel junctions were chemically etched in order to get physical access to the Ge BC. *Figure 3.6* shows the corresponding doping profiles of the three samples. Now the situation has changed considerably as compared with what was observed in *Figure 3.3*. For the three samples, the doping profile in the first “50-60nm” (gradual region) has changed as compared with the as-grown case, showing lower doping values.

Additionally, for nucleation B and C, the gradual region of the emitter is slightly deeper and the final doping emitter at the flat region is lower. Regarding the thickness of the emitter, nucleation B shows almost the same thickness as the conventional one ($\sim 270\text{ nm}$) while for nucleation C, a thinner emitter was achieved ($\sim 240\text{ nm}$). The doping increment (little hump) observed for nucleation B near the junction for nucleation B is considered as a measurement artefact.

Figure 3.6: ECV profile of Ge BC formation regarding the different nucleation routines after the whole growth of the TJSC structure. In order to get physical access to the BC the upper subcells were chemically etched.

TJSCs were manufactured on these three structures so their electrical performance could be compared. Both dark (Figure 3.7) and light I-V curves at 500 suns (Figure 3.8) show a significant improvement of $\sim 50\text{mV}$ in V_{OC} when nucleation B is used instead of the standard nucleation A. This improvement is virtually twice than that observed in Table 3.2 at one-sun for single junction devices. We interpret this associated to a higher resilience of sample B (as compared with sample A) to the thermal load associated with the growth of the middle and top subcells, which is the same in both cases. Looking back to Figure 3.6, such differences seem not to be related to emitter depth, which is similar in both samples, but to more subtle changes in the shape of the doping profile in the gradual region or on the maximum doping achieved in the flat region. Recent work in our group confirms that a severe degradation of the minority carrier collection properties at the gradual emitter region is the main mechanism behind the V_{OC} drop [Barrigón et al. 2017]. Thus, the thermal load reduction at nucleation B might result in a lower degradation of the aforementioned minority carrier properties in comparison with nucleation A.

The electrical behavior observed in the TJSC incorporating nucleation C presents a different evolution. Looking at the dark I-V curves (Figure 3.7), the presence of a significant series resistance is evident. This was confirmed with the subsequent light I-V curve taken at 500 suns (Figure 3.8), which indeed reveals the presence of a parasitic junction.

Figure 3.7: Dark I-V curves of the TJSC integrating nucleation A (conventional), nucleation B and nucleation C.

In order to interpret this result we should go back to Chapter 2, where Ge solid state diffusion was analyzed. As it was presented, when growing such thin nucleation layers, Ge was able to diffuse across the GaInP nucleation layer penetrating into the Ga(In)As buffer up to $\sim 215\text{nm}$ (see section 2.2.3). For this particular case, the 1000nm thick Ga(In)As was more than able to act as a barrier avoiding further Ge solid diffusion on active layers such as the tunnel junction. However, in sample C we have an extremely thin Ga(In)As buffer layer of only 50 nm . Subsequently, what we are possibly detecting in sample C is the result of Ge solid-phase diffusion reaching the tunnel junction and having deleterious effects on its properties. This is observed in both dark and light I-V curves where the presence of a high series resistance or a parasitic junction is observed.

Anyhow, even if nucleation C is not adequate to be incorporated in a complete TJSC, nucleation B has shown the most satisfactory result with a V_{oc} increase of $\sim 50\text{mV}$ (at 500 suns) in a complete TJSC structure, as shown in the inset of Figure 3.8.

Figure 3.8: Light I-V curves (~ 500X) of the TJSC integrating nucleation A (conventional), nucleation B and nucleation C.

3.2.4. Influence of Si₃N₄ back side coating

As a final part of this study, the impact of the use of a Si₃N₄ (~ 100nm) backside coating on the Ge wafers on the V_{oc} of the Ge BC was also evaluated. In this study our standard nucleation routine (i.e., sample A of the latter section) was used on two kinds of Ge wafers, one with a Si₃N₄ back coating and the other one uncoated (see Figure 3.9). Once more, to ensure that both processes were taking place at the same conditions, the wafer surface temperature was measured by pyrometry during each epitaxial growth and was confirmed to be the same for the two samples (see Figure 3.10).

Figure 3.9: Sketch of the Ge BCs analyzed with a) a conventional Ge wafer and b) a Ge wafer with a Si₃N₄ back coating of ~100nm.

Figure 3.10: Real temperature recorded by pyrometry of the semiconductor structures grown for both kind of Ge wafers (with and without a back Si_3N_4 coating of Figure 3.9).

As presented in section 2.2.4 of Chapter 2, the solid-phase diffusion of Ge into the III-V layers is more intense when a Si_3N_4 back coating is on the wafers. The mechanism we postulated to explain this behavior was that, in the case of coated wafers, the only available escaping path for Ge atoms was through the Ge/III-V interface. On the contrary, when no back coating was used, Ge atoms experience two opposing gradients, the one towards the front surface to feed diffusion into the III-V and the one towards the rear side of the Ge wafer where they are being etched away and evaporated. So the competition between these two escaping paths (from the front and back surface of the Ge wafer) resulted in a shallower Ge diffusion profile into the III-V layers in uncoated wafers.

In this section we are interested in understanding what happens in the reciprocal case, this is, how coatings affect the diffusion of group-III and group-V species into the Ge. Figure 3.11 shows the doping profile as measured by ECV in coated (red symbols) and uncoated (black symbols) wafers.

The use of this Si_3N_4 back coating results in a deeper emitter with a higher doping level. Conversely, the gradual region seems not so affected, though ECV provides little definition in this region. This result seems in good agreement with what was observed in Chapter 2. If a more intense Ge penetration into the III-V is observed in coated wafers, a higher availability of Ge

vacancies should be present for Ga, In and P to diffuse more intensively, as we observe. This more intense diffusion causes a deeper emitter in Si_3N_4 back coated wafers, but, as shown in the latter section, it is not the emitter thickness but the emitter minority carrier properties whose have the largest impact on BC V_{oc} .

Figure 3.11: ECV profile of Ge BC formation with similar nucleation routine but different Ge wafers (with and without a back Si_3N_4 coating). Red symbols represent the profile for Ge wafers with Si_3N_4 coatings, whereas black symbols represent the profile for Ge wafers without Si_3N_4 coating.

Figure 3.12: Dark I-V curves of Ge BCs with and without the use of a Si_3N_4 back side coating.

In order to assess the electrical properties, solar cells were manufactured on both wafers. *Figure 3.12* shows the comparison of the dark I-V measured in each case. From the dark I-V curves, the V_{OC} gain achieved with the use of the Si_3N_4 can be estimated to be of $\sim 15\text{mV}$, which is consistent with the results of the I-V curve summarized in *Table 3.3*.

Figure 3.13 plots the experimental IQE in both samples. The IQE from 300 to 700nm (GaInP absorption range) is almost the same in both samples in consistence with the analogous GaInP nucleation layer used for both structures (not shown here). However, changes in response are identified from 800 to 1200 nm where a slightly better response is observed when using a Si_3N_4 back coating. Such spectral range implies that the use of Si_3N_4 back coating improves the emitter response of the cell. The mechanism behind this improvement is still under investigation. A possible explanation for the improvement in the response of the emitter could be related to a cleaner diffusion (i.e. with less interstitial, precipitates, defects, ...) favored by the higher concentration of Ge vacancies, that would in turn produce better minority carrier properties. On the other hand, no change at the IQE of the base range is observed. All in all, as shown by *Table 3.3*, up to 1.4 mA/cm^2 gain in J_{SC} is achieved with the use of this back coating.

Figure 3.13: Internal quantum efficiency (IQE) of the BC with and without the use of a Si_3N_4 back side coating.

Table 3.3: Summary of the J_{sc} and V_{oc} parameters for the different Ge BC

<i>Ge wafer</i>	<i>GaInP nucleation</i>	<i>Ga(In)As buffer</i>	J_{sc} (mA/cm ²)	V_{oc} ⁴ (mV)
With Si ₃ N ₄	300nm at 680°C	350nm at 680°C	18.5	243
Without Si ₃ N ₄	300nm at 680°C	350nm at 680°C	17.1	229

3.3. Optimization of the GaInP subcell

3.3.1. Introduction

The development of the top GaInP subcell was studied in our group during the thesis work of Dr. García for its implementation in a GaInP/GaAs dual junction solar cell. That work resulted in a world record device [García 2010]. Some years later, this work was followed by the subsequent implementation and further development of the GaInP subcell in a TJSC [Barrigón 2014] which resulted in the TJSC presented in Chapter 1 with a 39.2% efficiency at 400 suns. This section of the Chapter is focused on additional optimizations of such GaInP subcell. Particularly, we have tackled this optimization pursuing two improvements: 1) the improvement of the V_{oc} through a better understanding and control of the ordering effect in GaInP using surfactant mediated growth with Sb; and 2) the improvement of its J_{sc} through the increase in the transparency of the window layer using strained AlInP layers with a higher Al content and higher AlInP doping. Accordingly, this section is divided into three main sub-sections. The first one continues the works of [Barrigón 2014] with the analysis of the use of Sb as a surfactant during the growth of the GaInP subcell base, focusing on the impact of Sb on GaInP microstructure. The second one describes the route followed to further disorder the GaInP subcell with the introduction of Sb in its emitter, since in our prior standard process GaInP:Sb was only used in the base. Finally, the third one presents the results about an AlInP window with improved transparency.

⁴ V_{oc} estimated from the dark I-V curves

3.3.2. On the use of Sb mediated growth in the TC GaInP base

GaInP, as many other III-V ternaries, shows CuPt ordering in the group-III sublattice. CuPt-type ordering describes a superlattice of alternating GaInP atomic layers with structure $\text{Ga}_{0.5(1-\eta)}\text{In}_{0.5(1+\eta)}\text{P}/\text{Ga}_{0.5(1+\eta)}\text{In}_{0.5(1-\eta)}\text{P}$, where η is defined as the order parameter. For a completely disordered GaInP material $\eta=0$, whereas for a completely ordered material $\eta=1$. So far, only experimental values as high as $\eta=0.6$ have been reported for GaInP grown by MOVPE [Ernst et al. 1995, Lee et al. 1999]. Despite there are four equivalent $\{111\}$ planes in the zinc-blende structure, ordering in GaInP grown on (001)-oriented substrates is only observed on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes (i.e., CuPt_B structure with two variants) as evidenced by a double periodicity in electron diffraction patterns obtained in $[110]$ cross-section views [Bellon et al. 1989, Gomyo et al. 1988]. Moreover, misorientation of the (001) substrate by a few degrees towards (111) favors the formation of only a single variant [Bellon et al. 1989].

The degree of order modulates, among others, the bandgap energy (E_g) of the alloy [Gomyo et al. 1988]. In order to increase the conversion efficiency of a MJSC, the band gap energy of the GaInP TC should be increased as much as possible [Garcia et al. 2008] or, in other words, to have a disordered GaInP TC. In fact, an increase as high as 160 meV in E_g (at low T) has been reported after decreasing the ordering degree [Stringfellow et al. 2000]. In order to control the degree of ordering, either epitaxial growth parameters are changed (such as growth temperature growth rate, V/III ratio, doping level, wafer off cut) [Copel et al. 1989, Lee et al. 1998, Lee et al. 1999, LeGoues et al. 1990, Massies et al. 1992], or surfactants are employed during the epitaxial growth [García et al. 2007].

In our group, a big effort was made in the quest of the optimum growth window for the GaInP subcell in terms of maximizing its morphological quality (smoothness, lack of hillocks,...). Therefore, there was little room to play around with growth parameters to achieve disordering. Accordingly, the use of surfactants during the epitaxial growth was chosen as the best mechanism to induce a change in the GaInP ordering [Barrigón 2014] and thus to enhance the GaInP efficiency [Barrigón et al. 2015, Olson et al. 2006]. Sb was chosen as the best candidate, since other possible surfactants (as Te or Bi) present some disadvantages such as a strong memory effect [García et al. 2007, Lee et al. 1998] or surface morphology deterioration [Stringfellow et al. 2000]. In addition, the incorporation of Sb in the solid is low, namely, around 10^{18} cm^{-3} [Olson et al. 2006] and it takes the place of P, with which is isoelectronic (i.e., it will not affect the band structure in a noticeable way for our application). As an important drawback, if excessive Sb is

used, the resulting GaInP layer will exhibit composition modulation and a triple period order which, in turn, notably lower the value of E_g [Fetzer et al. 2000, Stringfellow et al. 2000].

Preliminary photoluminescence (PL) measurements performed at RT on both n-type and p-type test GaInP layers (*Figure 3.14*) indicated that the n-type ($\sim 7 \cdot 10^{17} \text{ cm}^{-3}$ – $1 \cdot 10^{18} \text{ cm}^{-3}$) GaInP emitter was almost disordered (PL peak at 1.89 eV) while p-type ($\sim 1 \cdot 10^{17} \text{ cm}^{-3}$) GaInP was still partially ordered (PL peak at 1.82 eV). This was expected, since the doping level also modulates the degree of order [Kurtz et al. 1994, Stringfellow et al. 2000]. Thus, for the particular case of the GaInP structure used in our design, the emitter showed a low-order parameter as a result of its high doping level [Barrutia et al. 2015]. With this as a starting point, an intensive work was developed during the PhD Thesis of Dr. Barrigón with the aim of decreasing the GaInP base ordering with the use of Sb as surfactant during MOVPE growth. Since the effect of Sb was found to be very sensitive to growth conditions and reactor geometry —the surfactant action of Sb is determined by the amount of Sb that eventually reaches the growth surface—, an in-situ monitoring method was developed in our group based on RAS [Barrigón et al. 2015]. This monitoring enabled the calibration of the Sb molar flow that needed to be introduced during the growth of GaInP in the reactor chamber to achieve a desired order parameter.

In addition, from the layers grown with different Sb/P ratios, it can be observed (*Figure 3.14 b*) how the peak position shifts to higher energies as the amount of Sb is also increased, ranging from 1.819 eV up to 1.884 eV [Barrigón et al. 2015].

Table 3.4: Summary of the GaInP TC base layers with different amounts of Sb and the corresponding ordering degree obtained at [Barrigón 2014].

<i>Semiconductor structure</i>	<i>Sb/P (ppm)</i>	<i>η</i>
A	0	0.53
B	411	0.48
C	728	0.43
D	1720	0.29

Figure 3.14: (a) Normalized PL measurements at RT of two different test GaInP layers grown under the same conditions of the TC base (red) and TC emitter (black). (b) Normalized PL measurements at RT of GaInP TC base layers with different amounts of Sb.

3.3.2.1. TEM analysis of the GaInP base

Since no study on the microstructure of partially ordered GaInP alloys when employing Sb as a surfactant was found in the literature, we decided to undertake such. Moreover, despite electron diffraction and dark field (DF) imaging in conventional microscopy have been extensively used to analyze GaInP ordering, works revisiting III-V compound ordering within the dimension of aberration corrected atomic resolution scanning transmission electron microscopy (STEM) are very scarce [Wu et al. 2014].

Consequently, to complete this study, the impact of Sb on both the degree of ordering and the microstructure of GaInP layers was assessed by TEM. The TEM images in this section were taken at the Laboratory of Electron Nanoscopy (LENS) in Barcelona. The samples used for this study, were the same already used in relation with the PL measurements that have been briefly presented in Figure 3.14 b and described in [Barrigón 2014]. GaInP layers (Zn doped) simulate the GaInP base of our conventional TJSC. We used Ge(001) substrates with 6° misorientation towards the nearest [111]. They all consist of a 365 nm thick GaInP nucleation layer, followed by a Zn-doped, 1100 nm thick GaInP layer, where different amounts of Sb were introduced in the reactor to promote a surfactant mediated growth. Hereafter, this layer will be called the layer of interest (LOI) as presented in the following TEM images in Figure 3.15 a. The GaInP layers were grown at a nominal temperature of 675°C , with a V/III ratio of 120 and a growth rate of 0.60 nm/s.

For TEM characterization, structures were thinned up to electron transparency using a Focused Ion Beam (FIB) lift out procedure. Samples were prepared in the two orthogonal $[110]$ and $[1\bar{1}0]$ directions in order to unambiguously investigate the type of CuPt ordering existing in the layers.

Conventional dark field (DF) and selected area electron diffraction (SAED) observations were carried out in a JEOL 2100 operated at 200kV. An aberration corrected Titan FEI instrument operated at 300kV was used for high resolution high angle annular dark field imaging (HAADF) in scanning transmission (STEM) mode.

Conventional low magnification bright field TEM images, as the one shown in *Figure 3.15 a)* as an example, confirm the high quality of all samples. No trace of anti-phase domains —due to coalescence of zinc-blende phases typically encountered in III-V materials grown on group-IV substrates [Kroemer 1987]— was observed for any sample at the GaInP/Ge heterointerface (see *Figure 3.15 b)*). Therefore, we can discard any influence of the III-V/IV heteroepitaxy in the microstructure of the upper layers grown using Sb. In addition, no evidence of GaInP decomposition was found in any of the examined samples. This was avoided by the use of relatively low Sb/P ratios and high growth rates [Lee et al. 2001].

Figure 3.15: (a) General low magnification view in bright field mode of the semiconductor structures analyzed in this work. (b) HAADF image of the interface between the GaInP nucleation layer and the Ge substrate.

Accordingly, *Figure 3.16* shows the selected area electron diffraction patterns (SAED) of the LOI in the structures in cross-section geometry along the $[110]$ and $[1\bar{1}0]$ directions for the different Sb/P ratios employed. As it can be seen, all samples observed in $[1\bar{1}0]$ zone axis show the expected pure zinc-blende pattern. On the contrary, SAED patterns of all the $[110]$ oriented samples include extra satellite spots at positions $(h\pm 1/2, k\mp 1/2, l\pm 1/2)$. These results show the existence of a CuPt_B ordering in the $(1\bar{1}1)$ plane with only one variant for all samples, which indicates that Sb does not change the type of ordering (CuPt_A vs CuPt_B , or single vs double variant) that would be expected for GaInP grown on a highly misoriented substrate [Bellon et al. 1989].

Moreover, the variations in the degree of order among the different samples can be qualitatively inferred by comparing the ratio of intensities between the $1/2\{111\}$ superlattice spots and the

usual zinc-blend spots in the same diffraction pattern. As the Sb/P ratio is increased, the relative intensity of the $1/2\{111\}$ spot becomes weaker, which indicates that Sb is actually decreasing the order parameter (*Figure 3.16*). This is in good agreement with the decrease in η with Sb/P ratio reported by [Barrigón 2014] and summarized in *Table 3.4*.

Figure 3.16: Comparison of the selected area diffraction patterns of the LOI in the structures along the $[110]$ zone axis (top panels) and $[110]$ zone axis (bottom panels) as a function of the employed Sb/P ratio. Notice the superstructure reflections between the main spots in the direction parallel to $g = (1\bar{1}1)$ in the $[011]$ zone axis diffraction patterns only. The yellow arrow indicates the $[001]$ direction in all cases.

On the other hand, dark field electron microscope images were obtained using the satellite spot $(1/2, 1/2, 1/2)$. Looking at *Figure 3.17*, all samples present a single-variant domain structure separated by antiphase boundaries (APB) dark stripes. In the sample grown as a benchmark (i.e., Sb/P = 0 ppm), the APBs originate from the heterointerface GaInP/Ge with an antiphase boundary angle (θ_{APB}) lower than the value previously reported for GaInP grown on GaAs with the same offset (approx. 65°) [Su et al. 1994]. In this case, where no Sb is used, the nucleation layer cannot be distinguished from the buffer layer according to the microstructure (i.e. the orientation of the APBs is the same in both the GaInP/Ge nucleation layer and the LOI). On the contrary, θ_{APB} is significantly modified in GaInP once Sb is employed during the growth and therefore, a clear change in θ_{APB} is observable between the nucleation layer and the LOI (see *Figure 3.17 b*) and *c*). However, since unavoidable strain contrast and bend contours are present at the GaInP (nucleation)/GaInP:Sb (LOI) interface in these dark field imaging mode images, it is not possible to distinguish whether the APBs propagate from the nucleation to the LOI layers or new APBs are created just at the interface between them. *Figure 3.17 d*) shows the evolution of the average value of θ_{APB} versus the Sb/P ratio employed for the growth of the LOI. The θ_{APB} monotonically increases with the Sb/P ratio, reaching values higher than 90° for Sb/P ratios of 728 ppm. As far as we know, such high θ_{APB} values have only been observed in other materials such as in GaInAs

layers grown on InP [Ahrenkiel et al. 2001]. It should be noted that the quantitative relationship between θ_{APB} and Sb/P gaseous molar flow ratio found in this work has only an exemplary value since it depends on both reactor configuration and geometry. Yet, the trend is relevant.

Figure 3.17: Dark field TEM images obtained along the $[110]$ zone axes using the satellite spot $g=(1/2,-1/2,1/2)$ (a) with no Sb; (b) with a Sb/P ratio of 411 ppm; (c) with a Sb/P ratio of 728 ppm. (d) Schematic representation of the change in orientation of ordered domains (angle θ_{APB} as a function of Sb/P ratio).

An explanation of the growth dynamics originating these changes in θ_{APB} can be found elsewhere [Coll et al. 2017]. In addition, the microstructure of the domains and their boundaries was elucidated using high angle annular dark field (STEM-HAADF) imaging and simulations which can be found in [Coll et al. 2017].

As a summary of this section, the type of ordering observed for the Zn-doped GaInP layers presented in [Barrigón et al. 2015] is $CuPt_B$ single variant and it is unaffected by the use of Sb during the epitaxial growth, as shown from electron diffraction and HAADF data. The relative intensities of the $(h\pm 1/2, k\mp 1/2, l\pm 1/2)$ satellite spots related to the order became weaker with increasing Sb flux, in good agreement with the reduction of the order parameter as determined from previous PL measurements. Additionally, the antiphase boundary angle of the APBs also increases as long as the Sb/P ratio is further increased.

3.3.3. Sb-mediated growth of the n-GaInP-emitter

3.3.3.1. Introduction

In section 3.3.4 we will discuss the performance of the GaInP solar cells where Sb was only used to disorder the base layer [Barrigón 2014], in the belief that doping would be enough to do the job in the emitter. We will show in the aforementioned section that this idea is not correct and thus the use of Sb in the emitter needed is to be tackled.

3.3.3.2. Monitoring the effect of Sb in the GaInP emitter

The use of Sb as surfactant during the epitaxial growth of the n-type GaInP emitter was performed in a similar way as for p-type GaInP [Barrigón et al. 2015]. GaInP layers were grown at 665°C, with a V/III ratio of 120 and a growth rate of 0.7nm/s. Again, a 1.1µm thick, Si doped GaInP sample (with the same doping level as in the TC-emitter of the triple-junction solar cell) was grown on a Ge substrate. The thickness of the sample was chosen to avoid the Fabry-Perot interferences in the RAS signal at 665°C. Different amounts of Sb were introduced in the reactor under a constant molar flow of PH₃ ($1.79 \cdot 10^{-2}$ mol/min) during the growth of the Si-doped GaInP layer. Thus, the Sb molar flow introduced in the gas phase will be again expressed as the Sb/P ratio in parts per million (ppm).

The Sb/P ratios used in this study were in the range of the ratios used for the Zn-doped GaInP layers. DTBSi was used as the precursor for the Si dopant in the n-type GaInP layers and its flow was kept the same for all samples. As it will be shown in the following section, the final carrier concentration achieved in each layer after the introduction of Sb is almost constant and seems unaffected by the presence of Sb during the growth.

3.3.3.3. Effect of Sb on Si dopant incorporation

In addition to changing the ordering parameter, the use of Sb as a surfactant may produce some other collateral effects. For example, Sb impacts the composition of the GaInP alloy and increases the incorporation of Zn. This had been reported in literature [Chapman et al. 2006, Olson et al. 2006, Shurtleff et al. 1999] and it was also identified in our Zn-GaInP layers [Barrigón 2014]. Regarding the influence of Sb on the Zn incorporation, the carrier concentration was increased up to a factor 5 (red squares in *Figure 3.18*, which are results taken from [Barrigón 2014]). However, also in *Figure 3.18*, it can be appreciated how the carrier concentration of the Si-doped GaInP remains almost constant despite of the increase in Sb/P (blue circles in *Figure 3.18*). Our hypothesis for the explanation of this behavior is that the presence of such Sb atoms at the surface enables the incorporation of Zn atoms into the solid in a more energetically favorable way than P atoms. Consequently, for a specific Zn concentration used during the epitaxial growth, as long as the amount of Sb atoms being accumulated at the growing surface is increased, Zn incorporation will be enhanced. Thus, as long as Sb is increased, Zn incorporation is further increased until a saturation level is obtained (related to the specific DMZn flux introduced in the reactor chamber, see *Figure 3.18 a*, red squares). On the contrary, no significant change at the Si doping concentration is observed when Sb/P ratio is increased (*Figure 3.18 a*, blue dots). This behavior suggests that both Sb and P atoms are energetically equal for Si incorporation into the solid.

Figure 3.18: a) Carrier concentration achieved for Zn-doped GaInP (red squares) and Si-doped GaInP layers (blue circles) with the presence of Sb in the gas phase during the epitaxial growth. b) PL at room temperature of GaInP:Si layers as function of the Sb/P ratio.

Following with this argument, photoluminescence (PL) at room temperature reveals almost no change on the PL peak position of the GaInP:Si layers vs. Sb/P ratio. The energy change from the reference sample –with Sb/P=0– up to a Sb/P ratio of 1720 was from 1.898 eV up to 1.902 eV. Although Sb influence on GaInP:Si layers is lower, the slight shift to higher energies observed might be indicative of a higher disordering.

3.3.4. Characterization of the GaInP TC grown with Sb

3.3.4.1. EQE measurements

Previous studies in our group have shown how the band gap of the GaInP solar cell was effectively increased when Sb was introduced during the GaInP base epitaxial growth [Barrigón et al. 2016]. This can be observed by the shift in the EQE to lower wavelengths for higher Sb/P ratios (see Figure 3.19 a). In this first batch of samples, where Sb had been only introduced during the growth of the GaInP base, a little hump was observable in the EQE at high wavelengths (identified with a black circle in Figure 3.19 b)). In other words, in samples with high Sb/P ratios, instead of getting a sharp drop-off of the EQE, a little hump appeared when approaching E_g .

The relative influence of this hump in the integrated photocurrent was higher as the cutoff wavelength was decreased. In fact, for the sample with the highest Sb/P ratio (i.e., highest E_g), a current “gain” of 0.15 mA/cm² can be estimated as a result of this hump. The presence of such hump may be indicative of areas within the structure with a higher degree of order (i.e., lower E_g) than in the base layer. As Sb flow was only introduced during the growth of the base, the hump in the EQE could be the result of the emitter having a higher degree of ordering than the base

layer grown with high Sb/P ratios. Additionally, simulations⁵ of the TC EQE with an Sb/P ratio of 2610ppm at GaInP base revealed a GaInP emitter with an E_g of 25meV lower than the base [Barrigón et al. 2016].

Figure 3.19: a) EQE measurements of the GaInP/Ge dual junction solar cells with the different Sb/P ratios used during the GaInP base growth. b) Zoom view of the wavelength region where the little hump appears.

With the aim of getting rid of this hump, we performed a similar batch of samples where the Sb/P ratio had been varied along both the GaInP base and emitter. EQE and dark I-V curves were measured. In this way, both photocurrent and V_{OC} of the resulting solar cell were evaluated.

The semiconductor structure, together with the doping values and thickness of each layer are shown in Figure 3.20. We used the same semiconductor structure as in [Barrigón et al. 2016] in order to compare the solar cell performance when using Sb during the base growth only vs. base and emitter. In both situations the lattice mismatch of the samples was taken into account ($-125 < \Delta\theta < 0$ arcsec for all the samples).

In this batch of samples, a GaInP/Ge dual-junction solar cell without Sb was grown as a benchmark (sample A). As summarized in Table 3.5, some other samples (B to E) were grown with different Sb/P ratios in the emitter and base as well as growth interruptions between the emitter and base. Growth interruptions were incorporated in order to reset at some point the reactor conditions and to avoid the presence (carry over) of the high amounts of Sb used in the base at the beginning of the growth of the emitter. Table 3.5 summarizes these steps.

⁵ Simulations performed by Mario Ochoa

Figure 3.20: Semiconductor structure of the GaInP/Ge dual-junction solar cell employed to assess the effect of Sb introduction during growth of both GaInP base and emitter.

Table 3.5: Summary of the samples used in this study where Sb/P ratios have been modified and introduced during different steps of the GaInP epitaxial growth.

Sample	Sb/P (ppm)		Growth interruption between base and emitter	Important aspects
	Base	Emitter		
A	0	0	—	REFERENCE
B	2610	0	—	Sb off in the last 50nm of the TC_B
C	2610	0	2:00 in PH ₃	
D	2610	728	2:00 in PH ₃	
E	2610	2610	2:00 in PH ₃	

As evidenced by Figure 3.21, EQE measurements performed on these samples show the satisfactory reduction of this hump. A slight change can be appreciated from sample B to C (Sb only in the base). Nevertheless, it is not until Sb is also introduced during the growth of the emitter when the hump almost disappears. These results confirm that some regions of the GaInP emitter were presumably slightly ordered (lower E_g) than the already disordered GaInP base.

Moreover, it was mentioned that when Sb/P ratio is used during the GaInP base growth, it increases dopant incorporation (Zn) as it was shown in Figure 3.18. This higher Zn incorporation results in a lower EQE response (since the minority carrier lifetime of electrons in the base is decreased), which explains the lower absolute magnitude of the EQE of samples B (red), C (green)

and D (dark blue) in *Figure 3.21*. However, when DMZn flows are readjusted to obtain the targeted doping levels in the base, the EQE totally recovers (light blue curve in *Figure 3.21*) and virtually overlaps that of the reference cell except from the change in the cut-off wavelength.

Figure 3.21: a) External quantum efficiency of GaInP/Ge dual-junction solar cells for different Sb/P ratios. b) Magnification of the wavelength region where the little hump disappears.

Finally, it should be noted that the shift in the cut-off wavelength of the GaInP towards higher energies has direct consequences in the performance of the GaInP solar cell when it is employed as a top cell in a TJSC. The shift in the cut-off wavelength implies a decrease in J_{SC} since there is a significant loss in absorption in the range from 610 to 700 nm. For instance, a loss in J_{SC} of 0.67mA/cm^2 resulted when Sb was used for the growth of the base only. In these new experiments including the emitter, we estimate the J_{SC} loss to be 1.16mA/cm^2 for the AM1.5D ASTM G173-03 spectrum for the sample grown with a Sb/P ratio of 2610 ppm in both base and the emitter of *Figure 3.21* (with respect to the reference sample A). In order to compensate this loss in absorption and preserve the photocurrent, the top cell thickness base is typically used as an adjustable parameter to achieve current matching in an TJSC device [Kurtz et al. 1990]. In other words, the total thickness of the top cell is increased. However, this increase produces larger recombination currents, which in turn reduce the gains in V_{OC} . So we have two competing phenomena influencing the V_{OC} : the increase in J_0 and the increase in E_g . According to numerical simulations performed with Atlas-Silvaco⁶ and to previous work in our group [Barrigón 2014],

⁶ Simulations performed by Mario Ochoa

the net V_{OC} gain obtained would be positive, which justifies the use of Sb to enhance the efficiency of the TJSC. So, once incorporated in a TJSC architecture, the thickness of the GaInP base must be increased to counterbalance the current loss originated by the change in the energy bandgap. The performance of these TJSC will be assessed in Chapter 4.

3.3.4.2. Influence of Sb on the V_{OC}

The single publication found in relation with the use of Sb as surfactant during the growth of GaInP solar cells reported a V_{OC} increase of around 60mV [Olson et al. 2006]. Previous works in our group also confirmed that the gain in E_g when Sb (2610ppm) was used during the growth of the GaInP base of a dual GaInP/Ge solar cell produced a subsequent ~ 60 mV gain in V_{OC} [Barrigón 2014].

Figure 3.22: Dark I-V curves of GaInP/Ge dual junction solar cells with different Sb/P ratio on the GaInP top cell (base and emitter). Dashed lines correspond to the photocurrent of these devices at 1 and 10 suns considering a $J_{sc} \sim 9 \text{ mA/cm}^2$ at 1sun obtained from the integration of the EQE in Figure 3.21.

In this section, we study the dark I-V curves when Sb is introduced during the growth of both base and emitter regions of the GaInP TC. As an example, Figure 3.22 shows four GaInP/Ge dual junctions (as the one described in Figure 3.20) with a similar Sb/P ratio at the GaInP base (2610ppm) and different Sb/P ratio at the emitter (0, 178, 728 and 2610ppm). From the analysis of the dark I-V curves we can see that the V_{OC} increment caused by the introduction of Sb during the emitter growth, is almost unaffected for an Sb/P ratio of 178 ppm, while a V_{OC} gain up to ~ 15 mV is achieved when the Sb/P ratio amount at the emitter region was almost 5.7 times higher

(728ppm). These results, confirms that we need at least a Sb/P ratio of 728ppm during the emitter growth to see a slight increase at the V_{OC} related to an E_g gain of the emitter region. Regarding the I-V curve performance of the highest Sb/P ratio used in this study (2610ppm at the emitter region), we observe an unexpected behavior. We might associate this to processing problems during the electroplating step of the metal contacts formation. However, from these uncertainties observed, we cannot totally rule out the possibility of having an unexpected effect do to such high amount of Sb on the n-type layer. Thus, for the final TJSCs that will be presented in Chapter 4, we decided to decrease the Sb/P ratio down to 1400ppm at the GaInP emitter region.

3.3.5. Optimization of the AlInP window layer and GaInP emitter profile

With the aim of increasing the solar cell overall current collection, the aluminum content of the AlInP top cell window material was slightly increased [Jones-Albertus et al. 2015]. Of course, the idea behind this change is to increase the E_g of the AlInP window layer so that its absorption is minimized, allowing a greater amount of incident light into the GaInP n/p junction. Special attention should be paid during this aluminum variation. On the one hand, since the AlInP window is very thin, some degree of lattice-mismatch can be tolerated in this layer by distortion of the crystal lattice without forming crystal defects (i.e. forming a pseudomorphic layer). On the other hand, the critical thickness (which is defined as the thickness where the accumulated stress becomes energetically favorable to relax and relieve strain through the creation of a dislocation), depends upon many factors, including the materials involved, the substrate and/or underlying layers, growth technique and growth conditions. A critical thickness of around $\sim 15\text{nm}$ had been identified for a lattice mismatch of 1% with respect to the underlying layer and 50nm for a lattice mismatch of 0.4% [Wanlass 1990]. With all these facts, the Al content of the AlInP window (of $\sim 25\text{nm}$) layer was slightly varied between 0.8-1.3% with respect to the reference TJSC previously developed in our group.

Additionally, since the goal of these TJSC devices is to work under high concentration levels, the AlInP window doping level needs to be as high as possible. When doping densities higher than 10^{19} cm^{-3} are achieved in the AlInP window, the current is able to spread through it thus helping the emitter in the lateral current transport [Ochoa et al. 2016]. This can be accomplished with the use of Se and Te as dopants [Dai et al. 2015]. Thus, the precursor used in the AlInP window (DTBSi) was substituted by DETe. Moreover, the doping level at the GaInP emitter region had been also slightly modified. A higher doping level ($7\cdot 10^{17} - 3\cdot 10^{18}\text{ cm}^{-3}$ again with DETe) was achieved at the region close to the AlInP window interface and a lower doping level

($\sim 7 \cdot 10^{17} \text{cm}^{-3}$ with DTBSi) at the region close to the GaInP base. Therefore, a smoother transition to the high doping level in the window is achieved and a lower absorption takes place at the heterointerface due to the Burstein-Moss shift. Additionally, the emitter was reduced from 175nm down to $\sim 140\text{nm}$. The counterbalance between thickness reduction and the aforementioned doping profile modification, will result in a similar conductivity of the emitter layer with respect to the Reference one. The performance of these TC structures was assessed by EQE measurements (Figure 3.23). It should be notice that for this batch of TCs, the Sb/P ratio was not modified between Design A, B and C, and the thickness of the GaInP base was increased up to $\sim 1300\text{nm}$ for the Reference TC and ~ 1380 for Designs A, B and C. All these parameters are summarized in Table 3.6.

Table 3.6: Summary of the main parameters modified between the different TC structures of Design A, B and C with respect to the Reference one (REF).

TC Designs	Emitter/base Sb//P ratio (ppm)	GaInP Emitter		GaInP Base		AlInP window doping (cm^{-3})
		Doping (cm^{-3})	Thickness (nm)	Doping (cm^{-3})	Thickness (nm)	Thickness of 25nm
REF	0 // 2610	[Si] $\sim 7 \cdot 10^{17}$	175	[Zn] $\sim 9 \cdot 10^{16}$	1300	[Si] $> 1 \cdot 10^{18}$
A	1400//2610	[Si] $\sim 7 \cdot 10^{17}$	175	[Zn] $\sim 9 \cdot 10^{16}$	1380	[Si] $> 1 \cdot 10^{18}$
B	1400//2610	[Te] $> 3 \cdot 10^{18}$	24	[Zn] $\sim 9 \cdot 10^{16}$	1380	[Te] $> 5 \cdot 10^{18}$
		[Te] $> 7 \cdot 10^{17}$	70			Al composition increase of 0.8%
		[Si] $\sim 7 \cdot 10^{17}$	45			
C	1400//2610	[Te] $> 3 \cdot 10^{18}$	24	[Zn] $\sim 9 \cdot 10^{16}$	1380	[Te] $> 5 \cdot 10^{18}$
		[Te] $> 7 \cdot 10^{17}$	70			Al composition increase of 1.3%
		[Te] $\sim 7 \cdot 10^{17}$	45

Figure 3.23: a) EQE comparison between the Reference TC and Designs A and B. b) EQE comparison between Design B and C where Al composition was modified at the AlInP window layer. Differences between the Reference and Designs A, B and C are summarized in Table 3.6.

Figure 3.23 a, shows the EQE of the TC Reference (red squares) and Designs A (green squares) and B (blue squares). As expected, the little hump at higher wavelengths is reduced as the result of a higher disordering at the emitter region with the use of Sb during its growth (Design A and B). Regarding Design B, it exhibits a better response between 350-650nm. This region is where the response of both the AlInP window and the GaInP emitter are dominant and thus we attribute the gain to the slight reduction of the GaInP emitter thickness and the higher AlInP doping achieved (Burstein-Moss shift) with the use of DETe as well as the higher Al content used for this AlInP window.

Design C presents a similar semiconductor structure as Design B except for the Al composition at the AlInP window layer which was further increased. For Design B, a relative Al composition increase of 0.8% with respect to the Reference TC was calculated from the relation between the solid composition and the precursor partial pressures described in [García 2010]. Regarding Design C, the relative increase was of 1.3% with respect to the Reference TC. As it can be observed from Figure 3.23 b, a poorer EQE is achieved, possibly as a result of the full relaxation of the AlInP window layer. The resulting defects at the emitter/window interface increase the interface recombination velocity of the minority carriers and degrade the solar cell collection efficiency, as compared to Design B.

With all these observations, Design B presents the best EQE performance regarding the TC optimization in terms of Al composition, window doping level and emitter thickness. The integration of this design in a complete TJSC will be presented in Chapter 4.

3.4. Evaluation of p^{++} AlGaAs/ n^{++} GaInP tunnel junctions

3.4.1. Introduction

In a complete multijunction structure, each subcell is electrically series-connected by tunnel junctions (TJ) which are basically heavily doped p/n junctions. As a result of the n-on-p configuration of our TJSC, the p side of one subcell will be connected by the n side of the other subcell via the TJ. Several requisites are considered when designing a TJ. On the one hand, TJs should be optically transparent (high band gap materials are preferable) so light can pass through the TJ to be absorbed by the subcells underneath. On the other hand, TJs should not add significant series resistance to the device. To this end, a high peak tunneling current with a low voltage drop (i.e., a low equivalent resistance) is an important feature to be accomplished [Algora 2007].

Over the last years, different TJ designs have been investigated in our group. With the aim of developing a highly transparent and a highly conductive TJ device to be used when working at very high concentration levels, the previous p^{++} AlGaAs/ n^{++} GaAs TJ was substituted by a p^{++} Al_{0.30}Ga_{0.70}As/ n^{++} Ga_{0.51}In_{0.49}P TJ. This TJ will be used to connect the top GaInP subcell with the middle Ga(In)As subcell [Barrigón et al. 2014]. In this design we put special emphasis in understanding the effects of the thermal load on the I-V curve of the tunnel junction. With this aim, we grew test devices and annealed some of them to simulate the growth of the rest of the structure. Under these conditions, we reported a drop in the peak tunneling current from 996 A/cm² to 235 A/cm² and a slight increase of the equivalent resistance from $7 \cdot 10^{-5} \Omega \text{ cm}^2$ up to $1.4 \cdot 10^{-4} \Omega \text{ cm}^2$. Although some degradation is evident, the quality of this TJ design is high enough to work in the ohmic region of the TJ I-V curve under high concentration levels (> 15,600 suns) without being the limiting component of the TJSC. Additionally, due to the substitution of the GaAs cathode by the highly transparent GaInP cathode, a gain in J_{SC} at the middle cell of 0.56 mA/cm² (integrated over the AM 1.5D ASTM G 173-03 (1000 W/m²) was obtained [Barrigón et al. 2014].

3.4.2. Integration of the p^{++} AlGaAs/ n^{++} GaInP TJ in a triple junction solar cell

Despite the successful development of this high bandgap tunnel junction, after its incorporation in a TJSC structure we observed an important increase in the series resistance, as will be shown in *Figure 3.24*. In addition to the TJ, also the middle cell window was changed from n-AlGaAs to n-GaInP. GaInP is commonly used as the window material of the middle cell. Moreover it will avoid possible problematic heterojunction between n-GaInP cathode and the n-AlGaAs interface, and last but not least this window will reproduce the high band gap TJ structure presented in [Barrigón et al. 2014]. Therefore, we ascribed the series resistance increase to the formation of a possible detrimental heterojunction between any of the new layers and their interfacing layers. *Figure 3.24*, shows the comparison between two similar triple junction solar cells except for the TJ between the top and middle subcells and the aforementioned change in middle cell window. The triple junction solar cell wafers integrating the old AlGaAs/GaAs design (black symbols) and the new AlGaAs/GaInP design (red symbols) were grown in the same batch and were processed into devices simultaneously, and therefore growth-related drift and processing-related differences should be minimal. The bending of the I-V curve observed at high voltages in the red curve is undoubtedly due to a higher series resistance, which we hypothesized to be the result of a parasitic junction arising from the integration of the new layers in the complete TJSC structure. Focusing initially on the TJ, since this TJ is to be placed between the top cell (TC) and the middle cell (MC)

in a GaInP/GaInAs/Ge triple junction solar cell, the two problematic heterointerfaces could be either that between the TC BSF and the TJ anode (p side), or the MC window layer and the TJ cathode (n side). However, we could infer from previous analyses [García et al. 2012] that the heterointerface formed between the p^{++} AlGaAs anode and the p-AlGaInP TC BSF will not induce any problem (it is also present in the p AlGaAs/ n^{++} GaAs design). Additionally, with the change of the window layer in the MC to GaInP, on the cathode side we have a n^{+} GaInP/ n GaInP homojunction, which could not represent a problem either. Therefore, our focus regarding this series resistance problem was placed at the interface between the middle cell emitter (n GaAs) and the new middle cell window layer (n GaInP).

Figure 3.24 : Dark I-V curves of a triple junction solar cell integrating the new p^{++} AlGaAs/ n^{++} GaInP high band gap TJ (red circles) and a triple junction solar cell integrating the previous p^{++} AlGaAs/ n^{++} GaAs TJ (black squares). Reprinted from [Barrigón 2014].

With the aim of shedding some light on this problem, a new batch of TJs with different surrounding layers was grown, processed and measured. Figure 3.25 summarizes the different designs analyzed.

Design A is referred to as the reference sample where the high band gap TJ was integrated in a complete TJSC (such as the one in Figure 3.24 in red symbols). For the following designs, the main focus was put on the doping of the new nGaInP window layer, which was doped at higher levels by increasing the DTBSi precursor flow during its growth (design B), or by the change of the doping precursor to DETe in both the nGaInP window and the nGa(In)As emitter (design C). As a final design, the previous AlGaAs:Si window layer was used back but an additional n

GaInP:Si cap layer of a few nanometers was inserted between the n^{++} GaInP:Te cathode of the TJ and this n AlGaAs:Si window layer (design D). In this way, the “parasitic junction” speculated at the emitter and the new window layer of GaInP:Si, would be suppressed.

Figure 3.25: Sketch of the different surrounding layers at the high band gap TJ

Figure 3.26 summarizes the dark I-V curve of the designs in Figure 3.25. Both designs B and C overperform the reference design A. This suggests that when the doping of the window layer is increased, by means of higher DTBSi flow or by using DETe, the series resistance is decreased being this coherent with an enhancement of tunneling at the heterojunction. From Design C (red dots), we can detect the presence of a slightly higher series resistance than in Design B (green dots). This could be attributed to a worst behavior of the front grid metallization performed by electroplating. To confirm this behavior, more experiments should be performed. Due to the lack of time, Design C was discarded in this study while Design B will be introduced during the development of the final TJSCs (Chapter 4). On the other hand, Design D (blue dots) is not plotted on the same graph since it was processed in a second batch. Different photolithographic masks

were used, with a different solar cell area (1mm^2 in contrast to 6mm^2 used in designs B and C). *Figure 3.26 b*) shows the evolution of the dark I-V curves at high voltages where the series resistance seems to be again mitigated with design D.

Figure 3.26: (Left) Dark I-V curves of triple junction solar cells integrating the new $p^{++}\text{AlGaAs}/n^{++}\text{GaInP}$ high band gap TJ. Reference cell (black dots); design B with a highly doped GaInP:Si window layer (green dots); and design C with a highly doped GaInP:Te window layer and a n GaAs:Te emitter (red dots). (Right) Comparison of the reference design (black dots) and design D with n AlGaAs:Si window and a n GaInP:Si interface layer (blue dots).

3.4.2.1. Influence of barriers in TJ performance

Barriers are desirable to limit the out-diffusion of dopants from the TJ to surrounding layers and thus improve their resilience to thermal treatments [Hideo et al. 1988]. Nevertheless, in the light of the problems with heterojunctions discussed in the previous section we decided to undertake a study to assess the impact of using AlGaAs barriers in the TJ in the series resistance of the solar cell.

Figure 3.27: Structures of the highly transparent $p^{++}\text{AlGaAs}/n^{++}\text{GaInP}$ TJ tunnel junction with (design B) and without barriers (design A) studied along this chapter.

In order to compare the electrical performance of these two designs, a GaAs cap layer was grown on top of each structure to facilitate the formation of ohmic contacts. The thermal load that these TJs would suffer in a normal situation by the subsequent growth of the top subcell was emulated by thermal anneals. Thus, the resulting semiconductor structures A and B were cut into two pieces. One of them was annealed for 30 min under AsH_3 at 675°C to mimic the thermal load suffered by the growth of the GaInP TC. The four pieces (design A, design A-annealed, design B and design B-annealed) were then processed simultaneously to obtain tunnel diodes. Rectangular diodes ($250\mu\text{m}\times 250\mu\text{m}$) were processed with conventional photolithographic techniques. The front and back contacts were based on AuZn/ and AuGe/Ni/Au metal systems, respectively. The chemical etchants used for the mesa formation were NH_4OH (2:1:10) and HCl for the As and P-based semiconductors, respectively. The J-V curves were measured with the four-point probe technique to suppress the influence of the series resistance of the probes and wires on the measurements.

Figure 3.28: Dark I-V curves of the high band gap TJ with (circles) and without (squares) barriers. “As grown” TJ (in black symbols) were compared with the similar TJ structure after the thermal load produced by the growth of the rest of the TJSC structure (red symbols).

As can be seen in Figure 3.28, the electrical performance of the tunnel junction was severely deteriorated when the AlGaAs barrier layers were added (Design B). Even if the level of the peak current is higher when AlGaAs barriers are used, an increase in its series resistance is clearly observable together with a lack of linearity in the tunneling region of the J–V curves. Both these problems were also found in [García et al. 2012] when introducing similar barrier layers in p

AlGaAs/n GaAs tunnel junctions. In that work, simulations with Silvaco-Atlas associated such degradation with the heterojunction formed between the n AlGaAs barrier with the surrounding layers. Thus similar potential barrier (at the GaInP:Te cathode and/or the GaAs:Si buffer interface) might be also behind the effect observed at the high band gap TJ. All in all, after this results the use of barriers in our high bandgap tunnel junctions was discarded.

3.5. Summary and conclusions

Several paths for improving the performance of TJSCs have been assessed along this Chapter.

The degradation in the V_{OC} of the Ge subcell observed after suffering the thermal load associated with the growth of the complete TJSC encouraged us to explore new nucleation routines to mitigate such load. Growth parameters such as growth time and temperature were investigated. The thickness of the GaInP nucleation layer was reduced from 350nm down to 50nm. So, was the Ga(In)As buffer thickness from 1000nm to 500nm with a temperature reduction of this layer from 675°C to 600°C. These two main changes alleviated the thermal load which resulted in a V_{OC} gain up to 50mV (at 500suns). Additionally, it was found that very thin GaInP nucleation and Ga(In)As buffer layers –of 50nm– improved the V_{OC} of the Ge BC but a parasitic junction was formed with a high series resistance after its integration in a complete TJSC structure, as revealed from both dark and light I-V curves. This was related to the Ge solid-phase diffusion analyzed in Chapter 2, where very thin nucleation and buffer layers were not able to withhold the diffusion from the Ge wafer that will consequently affect the active layers on top such as the first tunnel junction. As a final step of this study, very preliminary results have revealed that the use of a back coating of ~100 nm of Si_3N_4 might influence the Ge out diffusion into the III-V semiconductor layers as well as on the in-diffusion of III-V materials (especially P) in the Ge wafer. A V_{OC} gain of 15 mV with the use of this Si_3N_4 back coating was achieved. The diffusion mechanism associated with this kind of coatings might improve the final minority carrier properties of the emitter, which improves the Ge subcell V_{OC} .

With the aim of improving the GaInP TC performance, an effective decrease in the cutoff wavelength in the EQE of the GaInP solar cell (i.e., an increase in the energy bandgap of the GaInP used) has been obtained with the use of Sb during the growth of the GaInP material. In addition, we demonstrated that both the degree of order of the solar cell emitter and base layers influence the shape of the EQE of the devices. By using Sb also during the growth of the emitter, sharp drop-offs in the EQE were obtained at higher bandgaps, with no residual response from

ordered phases. Moreover, EQE measurements also confirm that Sb does not seem to affect the minority carrier lifetime of the solar cells tested. The current loss originated by the change in the energy band gap (i.e., $1.16\text{mA}/\text{cm}^2$ when an Sb/P ratio of 2610ppm is used in both base and emitter regions) can be counterbalanced with the increase in GaInP base thickness in a complete TJSC architecture. From dark I-V curves, we estimate at least an Sb/P ratio of 728ppm that needs to be introduced during the emitter growth to see a slight increase of $\sim 15\text{mV}$ in V_{OC} . Additionally, the type of ordering observed on GaInP:Zn layers is CuPt_B single variant and it is unaffected by the use of Sb during the epitaxial growth, as shown from electron diffraction and HAADF data.

Following with the GaInP EQE enhancement, the aluminum composition of the AlInP window layer was slightly modified in order to find the best performance of this thin layer. In addition, the doping level of this layer was intentionally increased with the use of DETe as the dopant precursor.

As the last point of this Chapter, we have analyzed and understood the origin of the series resistance that we found in the past when trying to integrate high bandgap p AlGaAs/n GaInP tunnel junctions in our TJSCs. We have demonstrated that this problem was linked to the change in the window layer of the middle cell to n-GaInP (to make it compatible with the $n^{++}\text{GaInP}$ cathode). Several strategies have been demonstrated to overcome this problem including the use of higher doping levels in the GaInP window or using the old n-AlGaAs window with a thin $n^{++}\text{GaInP}$ capping layer. Moreover, the use of AlGaAs barriers in this high bandgap tunnel junction was explored, though not positive results could be achieved, so the recommendation is to suppress them.

Chapter 4

DEVELOPMENT AND CHARACTERIZATION OF THE IMPROVED TRIPLE-JUNCTION SOLAR CELL

4.1. Introduction

The reference GaInP/GaInAs/Ge TJSC developed in our group prior to this thesis, presented an efficiency of 39.2% at 400 suns. Since the goal of this thesis is to enhance the performance of this TJSC, several paths were followed to squeeze even more the efficiency of this device.

The aim of this chapter is to introduce all the improvements achieved and developed in the previous chapter (Chapter 3). These changes were basically the following:

1. Improvement of the top cell by further disordering the top cell GaInP emitter with the use of Sb during the growth, together with the optimization of the top cell AlInP window layer by increasing the Al content and doping level.

2. Integration of a high bandgap tunnel junction between the top and middle cells. Modification of the middle cell window layer (in terms of doping level or materials) with the aim of improving the interface with the GaInP:Te cathode.
3. Improvement of the Ge bottom cell by reducing the thermal load of the process using a thinner GaInP nucleation layer and a thinner GaInAs buffer (the latter grown at a lower temperature).

The triple junction solar cell previously developed in our group was taken as a reference or benchmark (named as Reference along this Chapter) for the development of the various TJSC designs. The different improvements presented along Chapter 3 are not integrated all together in a whole TJSC structure. Consequently, this set of improvements have been integrated at different epitaxial growths. In order to simplify the comprehension, three TJSCs named as Stage I, II and III will be presented along this chapter which correspond to these gradual modifications.

The development and growth of this batch of TJSCs was faced at the end of a Spanish MINECO project (Celso 42) which implied reduced time and resources to use the MOVPE reactor for the epitaxial growth of the solar cell structures as well as the lack of the required window of time to grow the desired number of epi structures. With all these facts, the TJSC batch was grown in a very short time and we were not able to grow and introduce all the desired modifications. Due to the aforementioned conditions, EQE was used as the guiding characterization between each iteration in the optimization process (between each Stage).

In the end, we were able to attain a TJSC with efficiencies above to 40%. Unfortunately, the improvement was lower than the expected for reasons that are still not well understood. The evolution in recombination current from Stage I to Stage III follows what we expected, but hides an unexpected loss as compared with the Reference. This result should be carefully analyzed in order to find the subcell behind this effect.

4.2. Stage I: Structure and EQE

4.2.1. Semiconductor structure

The main goal of Stage I, was to introduce the use of Sb during the growth of both the GaInP base and emitter layers to increase the energy band gap of the GaInP TC. Following the results

presented in Chapter 3, Sb was also introduced during the growth of the GaInP emitter. A Sb/P ratio of 2610 ppm was used to disorder the GaInP base, whilst a lower Sb/P ratio of ~1400 ppm was used during the growth of the emitter since, as discussed in the previous chapter, the high doping in the n-GaInP emitter made it almost disordered. Moreover, as it will be shown in the following section, this Sb/P ratio is enough to get rid of the residual absorption associated to ordered layers –i.e., the little hump– that was observed in the EQE of the TC at high wavelengths (Figure 3.21).

Regarding the rest of the semiconductor structure, no other significant changes were applied on this structure with respect to the Reference TJSC. The semiconductor structure corresponding to Stage I can be seen in Figure 4.1, where the layers unchanged are dimmed.

Figure 4.1: Semiconductor structure of the GaInP/GaInAs/Ge solar cell developed during Stage I. Layers that have changed from the Reference design have been highlighted, whereas unchanged layers have been dimmed.

4.2.2. External Quantum Efficiency

Figure 4.2 presents the comparison between the EQE of the top and middle subcells of the Reference design (red) and that of Stage I (black). The EQE of the BC is omitted to magnify the range of the x-axis where the changes applied are relevant, since no changes in the bottom cell were made at this stage. Anyhow, the EQE of the bottom cell at this first Stage will be shown in Figure 4.6 for completeness. As observable in Figure 4.2, and more clearly in the magnification view on the right corresponding to the area shaded in gray, the decrease of EQE at the cutoff wavelength is sharper in Stage I as compared with the reference design (i.e., the hump is not visible anymore). Therefore, it can be concluded that the disordering in the emitter in the TC has been successful.

As was suggested in Chapter 3, the higher values of E_g reached in the new TC demand an increase in the TC base thickness to maintain the values of the J_{SC} needed for current matching. Such increase was implemented in both devices –Reference and Stage I–, which had nominal thickness of $\sim 1300\text{nm}$ (Reference) and $\sim 1380\text{nm}$ (Stage I). The moderate increase in thickness of the TC of Stage I, produces the small increment of the TC EQE as well as the shift in the oscillations of the MC EQE. With this changes the short circuit currents obtained from the integration of the EQEs in Figure 4.2 are as indicated in the following Table:

Table 4.1: Short-circuit current density J_{SC} calculated from the convolution of the EQE with the reference spectrum (AM1.5d ASTM G173-03 normalized to 1000 W/m^2) for the Reference and Stage I cells.

$TJSC$	$J_{SC}^{Top\ cell}$ (mA/cm ²)	$J_{SC}^{Middle\ cell}$ (mA/cm ²)	CM_{middle}^{top}
Reference	10.99	11.18	0.98
Stage I	11.07	11.35	0.98
Difference with respect to the Reference	+ 0.08	+ 0.17	–

The influence of using Sb during the emitter growth can be identified by looking at the horizontal gray dashed lines marked in Figure 4.2 b). Due to the energy shift of the TC to higher energies, a J_{SC} loss of $\sim 0.28\text{ mA/cm}^2$ was estimated at the 650-700 wavelength range. All in all, the net balance at the TC (base thickness increase plus TC energy shift) resulted in a small J_{SC} increase of $\sim 0.08\text{ mA/cm}^2$ with respect to the Reference one (Table 4.1). At the same time, the energy shift of the TC to higher energies implies a J_{SC} gain of $\sim 0.31\text{ mA/cm}^2$ at the GaInAs MC in the 600-700nm wavelength range (slanted lines in Figure 4.2 b). This time, the net balance

(change in the middle cell oscillations plus the energy shift of the TC) resulted in a gain of 0.17mA/cm^2 for the MC (Table 4.1).

From this Stage I we can confirm the satisfactory shift and control of the GaInP TC energy band gap with the use of Sb in both the base and emitter. Accordingly, similar Sb/P ratios were used in the following Stages II and III.

Figure 4.2: a) Comparison between the EQE of the TC and MC from Stage I (black dots), and those of the Reference solar cell (red dots). b) Zoom of the EQE in a) in the range of the cut-off wavelength. Measurements were performed on solar cells without ARC layers.

4.3. Stage II: Structure and EQE

4.3.1. Semiconductor structure

The main goal of the second iteration represented by Stage II was the integration of the high band gap tunnel junction, aiming at reducing the problems detected with the parasitic series resistance of the Reference (as discussed in Chapter 3). In addition to this, a further improvement of the TC design was implemented, which consisted in using a gradual doping in the emitter, a higher doping and Al content in the window. All these changes are visually summarized in Figure 4.3 where the semiconductor structure of Stage II is depicted. Again, layers that have changed

from the Reference design have been highlighted in colors, whereas unchanged layers have been dimmed.

TJSC-Stage II

Figure 4.3: Semiconductor structure of the TJSC solar cell developed during Stage II. Layers that have changed from the Reference design have been highlighted, whereas unchanged layers have been dimmed.

Regarding the incorporation of the high band gap tunnel junction, different designs mitigating this series resistance problem were shown in Chapter 3. For Stage II we opted for increasing the Si doping in the GaInP:Si window layer (i.e., the so called Design B in Chapter 3), which yielded a better performance (see Figure 3.25 in Chapter 3).

Regarding the improvement of the GaInP TC, we targeted an increase in the current collection by increasing the bandgap of the AlInP window and by modifying the doping profile of the emitter. This design corresponds again to the TC Design B in Chapter 3 where an EQE enhancement was achieved (see Figure 3.23 in Chapter 3).

Table 4.2 summarizes the parameters modified in Stage II with respect to the Reference. The main changes described in this table correspond to the gradual doping level in the GaInP emitter, with

the use of DTBSi and DETe as the doping precursors, together with the Sb/P ratio used (the same as in Stage I). Additionally, the doping level of the AlInP window and the Al content with respect to the Reference cell have increased, as shown.

Table 4.2: Summary of the main parameters modified between the different TC structures (Reference and Stage II)

TC	Emitter/Base Sb//P ratio (ppm)	GaInP Emitter		GaInP Base		AlInP window (cm^{-3})
		Doping (cm^{-3})	Thickness (nm)	Doping (cm^{-3})	Thickness (nm)	
A (Reference)	0 // 2610	[Si] $\sim 7 \cdot 10^{17}$	~ 175	[Zn] $9 \cdot 10^{16}$	~ 1300	[Si] $> 1 \cdot 10^{18}$
Stage II	1400 // 2610	[Te] $> 1 \cdot 10^{18}$ [Te] $> 7 \cdot 10^{17}$ [Si] $\sim 7 \cdot 10^{17}$	~ 24 ~ 70 ~ 45	[Zn] $9 \cdot 10^{16}$	~ 1380	[Te] $\geq 5 \cdot 10^{18}$ Al composition increase of 0.8%

4.3.2. External Quantum Efficiency

Figure 4.4 shows the EQE of the Reference and Stage II, where Stage II exhibits a better response between 350-600nm. This region is where the response of both the AlInP window and the GaInP emitter are dominant and thus we attribute the gain to the gradual GaInP emitter and the higher AlInP doping achieved with the use of DETe precursor as well as the higher Al content used for this AlInP window.

Table 4.3 shows the J_{SC} produced by each subcell in the Reference design and in Stage II. As shown by this table, a perfect current matching has been obtained ($CM_{middle}^{top} \sim 1$). Moreover, as it can be observed from Figure 4.4 and Table 4.3, the photocurrent of both GaInP TC and GaInAs MC were increased with respect to the Reference by $\sim 0.5 \text{ mA/cm}^2$ (at 1 sun) and 0.31 mA/cm^2 , respectively. Obviously, the increase in the TC J_{SC} comes from the improvements just discussed whereas the origin of the increase in the MC J_{SC} is the higher transparency of the upper layers in Stage II, originated by a TC with higher bandgap and a lower absorption in the highly doped window in the MC (Burstein-Moss shift).

Table 4.3: Short-circuit current density J_{SC} calculated from the convolution of the EQE with the reference spectrum (AM1.5d ASTM G173-03 normalized to 1000 W/m^2) for the Reference and Stage II.

TJ_{SC}	$J_{SC} \text{ Top cell}$ (mA/cm^2)	$J_{SC} \text{ Middle cell}$ (mA/cm^2)	CM_{middle}^{top}
Reference	10.99	11.18	~ 0.98
Stage II	11.49	11.49	~ 1
Difference with respect to the Reference	+ 0.50	+ of 0.31	—

Figure 4.4: EQE measurement of the GaInP and Ga(In)As subcells from Stage II (blue squares), together with the EQE of the Reference solar cell (red squares). Measurements were performed on solar cells without ARC layers. The EQE of the bottom cell is omitted to magnify the range of the x-axis where the changes applied are relevant, since no changes in the bottom cell were made at this stage.

4.4. Stage III: Structure and EQE

4.4.1. Semiconductor structure

In Chapter 3 we demonstrated an improvement of almost $\sim 50\text{mV}$ (at 500 suns) in the V_{OC} of the Ge subcells by means of the use of a thinner GaInP nucleation layer (50 nm at 675°C) and a thinner Ga(In)As buffer layer grown at a lower temperature (500 nm at 600°C). The incorporation of this new nucleation routine was the goal of Stage III. All the changes implemented at this new stage are visually summarized in Figure 4.5.

Regarding the GaInP TC design, no changes were implemented being identical to that of Stage II. Consequently, 1) a Sb/P ratio of 2610ppm was used to grow the p-GaInP base whilst a Sb/P ratio of 1400ppm was used to grow the n-GaInP emitter; 2) a gradual doping profile was used in the emitter; and 3) the Al content in the AlInP window layer was increased by 0.8% and its doping level was raised to $>5 \cdot 10^{18} \text{ cm}^{-3}$.

Finally, a minor change was implemented in the high bandgap tunnel junction. Following the analysis in Chapter 3, the n-GaInP:Si window layer for the MC used in Stage I (n^{++} -GaInP:Si in

Stage II) was substituted by a n-AlGaAs:Si of $\sim 30\text{nm}$, capped with a thin layer of GaInP:Te of $\sim 20\text{nm}$. This modification corresponds to TJ Design D from *Figure 3.25* (Chapter 3).

Figure 4.5: Semiconductor structure of the GaInP/GaInAs/Ge solar cell developed at Stage III. Layers that have changed from the reference design have been highlighted, whereas unchanged layers have been dimmed.

4.4.2. External quantum efficiency

The EQE of the TJSC developed at Stage III is shown in *Figure 4.6*. The curves of the top, middle and bottom cells are plotted (in green) together with those of the Reference (in red). As expected, the EQE of the TC is very similar to that of Stage II as a result of the lack of significant changes. In this occasion the integrated current is slightly lower probably due to measurement tolerances or MOVPE run-to-run variability. The EQE of the MC shows a small variation in the oscillation pattern as compared to the reference cell. This variation can be related to the effect on optical interference of the different materials and thicknesses used in the MC window, or a slight unintended change in top cell thickness (that could also explain the decrease in TC J_{sc}). Anyhow, the integrated current is within the expected range and, in fact, slightly higher than in Stage II. Thus, the current matching ratio in this design turns to be $CM_{middle}^{top} \approx 0.97$.

Table 4.4: Short-circuit current density J_{SC} calculated from EQE measurements (Reference and Stage III)

TJ_{SC}	J_{SC}^{Top} cell (mA/cm ²)	J_{SC}^{Middle} cell (mA/cm ²)	CM_{middle}^{top}
Reference	10.99	11.18	0.98
Stage III	11.29	11.58	0.97
Difference with respect to the Reference	+ ~0.3	+ ~0.4	—

Moreover, the EQE of the BC of the different Stages and Reference design have been plotted in Figure 4.6. Both the Reference, Stage I and II had a conventional nucleation routine. The aforementioned new and thinner nucleation routine was incorporated during Stage III. As it can be observed, all EQEs are very similar and no evident difference stands out after the integration of the new nucleation routine. In fact, J_{SC} reaches values close to ~14 mA/cm² in all cases. This result is in agreement with what was observed in chapter 3 when changes in the nucleation caused almost no effect in the collection efficiency (Figure 3.5) but produced a noticeable effect in the dark I-V (Figure 3.4). This will be also the case in the cells of Stage III as will be shown in the next section.

Figure 4.6: EQE measurement of the GaInP and Ga(In)As subcells from Stage III (green dots) and the Reference (red symbols), together with the EQE of the Ge bottom cell for the three Stages and the Reference. Measurements were performed without ARC layers.

In these sections, the EQE of these new structures has been presented. In particular, Stages II and III have shown very similar performance, with a clear improvement from the Reference design. In order to fully assess the efficiency potential of the new designs, in the following sections, dark and concentrator illumination performance will be analyzed.

4.5. Dark I-V measurements of Stage I, II and III

In the latter section, EQE measurements were presented as the checking way we use to move from one Stage to another since EQE only requires a fast and simple manufacturing process of the solar cells. In order to perform dark and concentration illumination measurements, solar cells from the three Stages were manufactured, with an active area of 0.06 cm^2 , using standard photolithography techniques and gold electroplating for the formation of the metal contacts. Unfortunately, no piece of the Reference structure was left to include it in this manufacturing batch. *Figure 4.7* shows the dark I-V curves of such cells. This figure reveals that recombination currents in Stages I and II are very similar. As expected, a lower series resistance is observed at high voltages for Stage II (due to the increase of the doping level of the GaInP:Si layer). Additionally, when the new nucleation routine is introduced in Stage III, a lower recombination current can be observed. Since the full dark I-V curve shifts towards higher voltages and does not overlap in any voltage range with the previous Stages I and II, we could infer that a decrease in the recombination current of the BC (J_{01}) has been achieved, which in turn should result in a better V_{OC} [Espinet 2012]. This is in line with the expected increase in V_{OC} targeted when implementing the new nucleation routine for the Ge bottom cell described in Chapter 3.

Figure 4.7: Dark I-V curves of the TJSC developed at Stage I, II and III.

All in all, *Figure 4.7* represents a step forward in the confirmation of the good integration of all the changes introduced and developed in our new TJSC designs. However, this figure is not fully satisfactory since it lacks of information about the Reference design. To check the Reference, we only had 1mm² solar cells, manufactured some years back, following the standard high concentrator processing of IES-UPM. In this sense, wafer pieces from Stages II and III were processed into solar cells with same size following the same technological steps (photolithography, thermal evaporation of the metal contacts, mesa etching via wet etching and the subsequent wire bonding and encapsulation processes). Similar metallization as those used in the Reference design were deposited as both the back (Au) and front contacts (AuGe/Ni/Au). We did not include Stage I, in this comparison, to minimize the experimental effort, since it shows the same performance as of Stage II (*Figure 4.7*).

Figure 4.8: Dark I-V curves of 1mm² concentrator TJSCs from Stage II (blue dots), Stage III (green dots) and the Reference TJSC (red dots).

Figure 4.8 shows the dark I-V curve of the solar cells from this batch (Stage II in blue dots and Stage III in green dots) in comparison with the dark I-V curve of the Reference TJSC (in red dots). As it is observed, Stage II and III do follow the expected tendency already presented in *Figure 4.7*, namely, a clear improvement in the recombination currents of Stage III. However, their performance with respect to the Reference is not what we expected. In terms of recombination, the Reference design should be very similar to Stage II (and I) since no significant changes have been made in the junction. Even more so, Stage II should present a slightly lower dark current as a result of the higher bandgap in the top cell. On the contrary, that is not the case in *Figure 4.8*,

which shows a deterioration of the recombination current in Stage II; then Stage III does represent an improvement but not as high as was forecasted.

In brief, the compared analysis of *Figure 4.7* and *Figure 4.8* reveals that the evolution in recombination from Stage I to Stage III follows what we expected, but hides an unexpected loss as compared with the Reference, and thus anticipates a reduction in the gains expected in V_{OC} .

4.6. Concentration response: Stage II and III

Concentration measurements were performed using a flash lamp based solar simulator (Helios 3030). For a detailed explanation of the concentration set-up and the measurement procedure, the reader is referred to [Domínguez 2012].

Isotype cells were used to provide information about the irradiance level and the spectrum impinging (E_i) our device under test. The Isotype cells are calibrated at AM1.5d ASTM G-173-03 (1000W/m^2), which means that they are perfectly current matched for this spectrum ($I_{sc,TC}^{isotype}(E_{AM1.5D})/I_{sc,MC}^{isotype}(E_{AM1.5D})=1$). Thus, by calculating the spectral matching ratio (SMR) which is defined by *Eq. 4.1*, for a unknown spectrum (E_i), we can determine at which irradiance level we have the equivalent AM1.5d ASTM G-173-03 (SMR=1) [Domínguez 2012] .

$$SMR = \frac{I_{sc,TC}^{isotype}(E_i)/I_{sc,MC}^{isotype}(E_i)}{I_{sc,TC}^{isotype}(E_{AM1.5D})/I_{sc,MC}^{isotype}(E_{AM1.5D})} \quad \text{Eq. 4.1}$$

Regarding the BC, it will always have a photogenerated current higher than both the TC and MC. This is because the flash lamp used is a Xenon lamp which is infrared rich (as it occurs in the AM1.5d spectrum). Therefore, the BC is not going to be the limiting subcell in any case. Accordingly, measurements were performed by searching SMR=1 for the TC/MC at each concentration level. In such way, we ensure that the measurements are performed at an equivalent AM 1.5d spectrum (1000W/m^2).

Figure 4.9 illustrates the V_{OC} versus concentration behavior of the Stage II and III cells in comparison to the Reference one. The evolution of open circuit voltage vs. concentration does not follow the expected trend (plotted in solid lines) for Stages II and III. Instead of that, the followed trend is that anticipated by the dark I-V curves in *Figure 4.8*. A V_{OC} drop of $\sim 20\text{mV}$ is observed at Stage II (blue squares) with respect to the Reference (red stars). Conversely, we

expected a gain of $\sim 10\text{-}15\text{mV}$ with respect to the Reference due to the bandgap increase associated with the incorporation of Sb at the emitter. This means that the total “missing” V_{OC} in Stage II is of $\sim 30\text{-}35\text{ mV}$. Additionally, since this V_{OC} loss is also present at Stage III (green triangles), the expected gain of $\sim 50\text{mV}$ with respect to the Reference is reduced in this case to a more modest gain of $\sim 15\text{mV}$.

Figure 4.9: V_{OC} versus concentration ($\times$) curves for the Reference (red stars), Stage II (blue squares) and Stage III (green triangles). Measurements performed on solar cells without ARC layers. Solid lines correspond to the expected V_{OC} trend for Stages II and III.

4.7. Discussion: Where is the missing V_{OC} ?

In order to understand the problem behind the unexpected dark I-V curves from Figure 4.8, and V_{OC} vs concentration curves in Figure 4.9 we present in this section our analysis of the situation. From Figure 4.7 and from the relative change in V_{OC} between Stage II and Stage III in Figure 4.8, we can conclude that the expected improvements between different stages are occurring as expected (i.e., increases in photocurrent and decreases in dark current). However, it is the starting point that is different; Stage II (and I) exhibit a V_{OC} which is $\sim 30\text{-}35\text{mV}$ lower than the Reference, as a result of their higher recombination currents. Essentially, we can outline four basic hypothesis to account for such loss:

1. Hypothesis 1: minor structural changes are behind the loss

We have introduced a number of minor changes from Stage I to Stage III (higher Al content in the TC window, gradual doping in the TC emitter, changes in doping and composition in the MC window, ...). It might well be that one or several of these changes, which we initially thought as neutral in terms of recombination, have an impact on dark current.

2. Hypothesis 2: Sb in the emitter is behind the loss

All stages from I to III share a fundamental difference with the Reference design, namely, the use of Sb at the TC emitter. It could be possible that Sb increases the surface recombination velocity at the window/emitter interface or deteriorates the minority carrier lifetimes at the TC emitter and thereby increases its recombination.

3. Hypothesis 3: general degradation in material quality is behind the loss

The Reference structure and those of Stage I to III were grown in the same MOVPE reactor but with a time difference 18+ months. Maybe, the general material quality degraded over this period because of a more contaminated reactor, older precursors and hydride sources or lower quality Ge wafers...

4. Hypothesis 4: unintentional changes in the doping of p/n junctions are behind the loss

Recombination currents are heavily dependent on the doping of the junction. In particular, an unintentional decrease in the doping concentration of the lightly doped base in the top cell could account for the loss in V_{OC} .

In the following, we revisit our experimental evidence in order to either support or challenge these hypotheses.

4.7.1. Evaluation of Hypothesis 1:

Is the loss coming from minor changes?

In order to assess the validity of this hypothesis we may go back to the dark I-V curves from *Figure 4.7*. From this figure, as the dark I-V curves from Stage I and II are virtually identical, we can discard the possible negative influence from the changes introduced between Stage I and II (such as the TC improvement with a higher Al content and a higher doping level at the AlInP, and the slight modification of the emitter doping profile and thickness). In this line, the introduction of the new nucleation routine at Stage III produces the expected reduction in recombination current so it seems that the shorter nucleation works and the change in the MC window as

compared to Stage II and I has no effect in the dark current. We therefore conclude that hypothesis 1 has little chance to be behind the loss.

4.7.2. Evaluation of Hypothesis 2:

Is the loss coming from the use of Sb in the TC emitter?

Obviating the new nucleation of Stage III, the big change from the Reference design and the three Stages is the use of Sb in the TC emitter. In order to check whether this change has an impact on the dark current, we should compare the dark I-V (and ideally the concentrator response) of top cells with and without Sb in the emitter. This evidence was presented in Chapter 3, where also the EQE of the devices was discussed (see *Figure 3.21* and *Figure 3.22*). However, the devices analyzed in Chapter 3 were not triple junction solar cells. It is unlikely though possible that the memory effects that take place in a long MOVPE growth such as a TJSC might have an impact on how the use of Sb affects the recombination current. In order to further understand these differences, we are going to carry out TEM measurements on these samples to see any effect at the microstructure or interface at the GaInP base and emitter regions. Moreover, to understand the I-V curves from *Figure 4.8*, spectral EL measurements are underway. With this characterization technique, we will have access to the individual I-V curve of each subcell in the TJSC and this will help us understand better which subcell is responsible for the loss in V_{OC} .

4.7.3. Evaluation of Hypothesis 3:

Is the loss coming from general degradation in the minority carrier parameters?

The Reference structure and those of Stage I to III were grown in the same MOVPE reactor but with a time difference 18+ months. Maybe, the general material quality degraded over this period because of a more contaminated reactor, older precursors and hydride sources or lower quality Ge wafers... In this way, the PV quality of all subcells (particularly the TC and MC) could suffer from a general deterioration of minority carrier parameters. Such a degradation would need to be high enough as to justify the loss in V_{OC} , but not so significant as to produce a noticeable change in the EQE, which even improves in some designs as observed in Chapter 3. The magnitude of the loss (~30-35mV missing between the TC and MC) makes it possible to reconcile this insensibility of the collection efficiency and effect on the recombination.

For the proper assessment of this Hypothesis 3, a copy of the Reference structure should have been grown in the same series of MOVPE runs that produced Stages I to III. In this way, any difference between old and new reactor conditions could have been traced. Unfortunately, due to time restrictions this was not the case, so we do not have a structure to compare. Anyhow, the measurement of the spectral EL, as discussed in hypothesis 2, will help discriminate this possibility.

4.7.4. Evaluation of Hypothesis 4:

Is the loss coming from unintentional changes in the doping of p/n junctions?

The recombination current in the neutral regions (J_{01} term) of a pn junction is, in a first approximation, inversely proportional to the doping in that region. If we consider that the J_{01} of both the middle and top cells is going to be mostly determined by the base, then changes in the base doping of either (or both) junctions could account for the missing ~30-35 mV. For example, a decrease in doping in the TC p-GaInP base from $1.8 \cdot 10^{17} \text{cm}^{-3}$ to $5 \cdot 10^{16} \cdot \text{cm}^{-3}$ (a reduction by a factor of ~3.5) would be enough to justify the full extent of the loss in V_{OC} . Obviously, the drop in base doping could be much smaller if both the MC and TC were affected and contributed to the loss. As we discussed in Chapter 2, Ge autodoping is a phenomenon that needs to be compensated for very accurately in order to obtain the desired Zinc doping in the base. It is possible that such compensation in this set of runs was not optimum and the resulting base doping was lower than expected. This would create little impact in the EQE but an evident loss in V_{OC} .

4.7.5. Discussion summary

In brief, we have several open possibilities to find the missing ~35mV in the V_{OC} . As of today, we are inclined to think of hypothesis 3 and 4 as the most plausible causes. New experiments are ongoing and probably spectral EL measurements will be the key to understanding the increased recombinations that we have found in the new structures.

4.8. Final efficiency results

Despite the fact that the missing V_{OC} is going to “eat” much of the improvement expected from the tuning made in the TJSC structure, we decided to finish some devices and get an efficiency

result. Therefore, to complete this study, anti-reflection coating layers were deposited on some of these final devices. Typical ARC layers used at IES-UPM are a ZnS/MgF₂ stack with thicknesses of ~ 40-50nm for the ZnS and ~ 80-100nm for MgF₂. As an example of the results after ARC deposition, *Figure 4.10* shows the EQE of Stage III after the deposition of the ARC layers. Anyhow, due to the lack of time, a careful optimization of the ARC to find the most suitable combination in terms of thickness was not performed and it will be carried out in a near future.

Figure 4.10: EQE measurements of TJSC Stage III and Reference with ARC layers.

Concentration measurements of TJSCs from Stage II and III with ARC layers were performed at IES-UPM. *Figure 4.11* shows the results of some of the best devices at ~416 $\times$. Due to the loss in V_{OC} , the efficiency gain with respect to the Reference is lower than expected. Nevertheless, these results confirm the good performance of these devices with an increase in efficiency of 0.7-0.8% absolute from the Reference solar cell. Moreover, both Stages II and III present efficiency values near 40% at ~416 $\times$, with Stage II exceeding 40%. These results could have been even better (around 40.7%) if Stage III didn't present a low FF of 82.9%, more than 1.5% lower than Stage II. We believe this drop is related to a higher series resistance in its front metallization originating from a processing problem in this particular wafer. This latter problem has been already tackled and solved in a recent Thesis in our group [Huo et al. 2017]. In this work, a new front grid metallization was developed based on Pd/Ge/Ti/Pd/Ag with a specific metal/semiconductor contact resistance $\rho_{MS} < 10^{-6} \Omega \cdot \text{cm}^2$ and a metal sheet resistance $R_{M,\square} < 40 \text{ m}\Omega/\square$. Both these values are more than an order of magnitude lower than those from the

conventional AuGe/Ni/Au metallization used in this thesis and were able to produce FF in concentrator TJSCs close to 90% from 200 to >1000 $\times$.

Obviously, a second line of action would be the recovery of the missing ~30-35mV in the V_{OC} . Such accomplishment would boost efficiency of Stage III to $\eta \sim 41.2\%$, very close to the world record for this technology.

Figure 4.11: I-V curves of the TJSC Stage II, III and the Reference under 415.8 $\times$. Solar cells with ARC. Measurements performed at IES-UPM.

Chapter 5

ELECTRO-OPTICAL PROPERTIES OF GRAPHENE FOR PHOTOVOLTAIC APPLICATIONS

5.1. Introduction

Graphene has reached an enormous interest and development during the last decade, due to its unique physical, mechanical and chemical properties. Despite graphene properties, such as the electronic structure, were already theoretically studied by P.R Wallace in 1947 [Wallace 1947], together with the wave equation and the similarity to Dirac equation presented some years later by [DiVincenzo et al. 1984, McClure 1956, Semenoff 1984] , it was not until 2004 when Andre K. Geim and Konstantin S. Novoselov were able to isolate one single layer of carbon from graphite, transfer it to a substrate and perform for the first time very interesting electrical measurements [Novoselov et al. 2004]. This paper not only put them onto the road to the Nobel Prize in Physics in 2010, but it was the starting point of a new optoelectronic world with a huge range of possibilities due to the development of new materials with unusual properties: the Two-Dimensional (2D) crystalline materials.

2D materials such as graphene, are mainly one-atom-thick materials that present exceptional properties which are generally different from its 3D properties. The 2D family is formed by a variety of materials that includes zero band gap materials (i.e., graphene), semiconductors (i.e. MoS₂) and insulators (i.e., hBN). These materials by themselves have very unique properties as already mentioned. But it is also important to remark that the combination of monolayers of these materials in vertical stacks built by van der Waals (vdW) forces can generate multilayers with new properties and thus expand potential uses even further [Fang et al. 2014, Wang et al. 2015, Withers et al. 2015] .

As it has been briefly presented, 2D materials will have a revolutionary impact in the near future in a lot of optoelectronic devices. In relation to this, one goal of this Thesis was to study the electro-optical properties of graphene for its integration on a lattice matched triple junction solar cell (TJSC) and to explore for the first time its benefits in order to enhance the solar cell efficiency.

With this aim, the work presented along this Chapter is focused on a deep characterization of the electrical and optical properties of graphene for its application in the field of MJSC working at high concentrations (~1000×). For this purpose, graphene grown by Chemical Vapor Deposition (CVD) has been used. Several aspects like the transfer process of graphene to the substrate of interest, the influence of the surrounding atmosphere, the photolithography process, etc, constituting the solar cell manufacturing process have been carefully studied in order to preserve graphene properties. This is compulsory since graphene is basically made up of one atom thick material and as it will be presented along Chapters 5 and 6, the impact of external agents affects strongly its behavior.

5.2. What is Graphene?

Graphene is a single layer of carbon atoms packed or arranged in a hexagonal honeycomb like pattern through sp² bonding with a thickness of 0.335nm (see *Figure 5.1*). The atomic distance between each carbon atom (C-C bond length) is ~ 0.142nm.

It is well known that carbon has an atomic number of 6. Two electrons are in the inner core and four electrons in the outer shell. Since graphene presents sp² hybridization, each carbon atom in graphene has three equal sp² lobes pointing outwards in a plane and connecting to adjacent carbon atoms. The fourth electron in this outer shell occupies a pi orbital that projects above and below the molecular plane (freely available in the third dimension as can be seen in *Figure 5.1 b*). This

pi orbital overlaps with adjacent pi orbitals which allows an easy movement of electrons across the graphene sheet giving rise to its remarkable electrical conductivity [Bunch et al. 2008].

Figure 5.1: a) Single layer of graphene, molecular structure. b) Sketch of the sp^2 hybridization present in graphene. Reprinted from^{7 8}.

All these characteristics allow graphene to present very interesting properties like Quantum Hall effect at room temperature, Klein effect, transparency and flexibility together with mechanical strength, impermeability and exceptionally high thermal and electrical conduction [Castro Neto et al. 2009, Chang et al. 2013, Geim et al. 2007]. Very high mobilities of $\sim 120,000$ - $15,000$ cm^2/Vs (at 240K) have been achieved, [Geim et al. 2007, Wang. H et al. 2012] and up to $200,000$ cm^2/Vs in suspended graphene [Du et al. 2008] .

Graphene is a zero band gap material and its electronic structure (band diagrams) consists of double cones (see Figure 5.2). For intrinsic graphene (undoped) the Fermi level is at the joint of the cones which is called the Dirac point. The density of states at the Dirac point is zero, increasing linearly for energies above or below it which allows for current conduction. Close to the Fermi level, the dispersion for electrons and holes is linear. Since the effective masses are given by the curvature of the energy bands, the Fermi level corresponds to zero effective mass. The equation describing the excitations in graphene is formally identical to the Dirac equation for massless

⁷ www.sciencenews.org

⁸ http://wps.prenhall.com/wps/media/objects/724/741576/Instructor_Resources/Chapter_01/Text_Images/FG01_15.JPG

fermions which travel at a constant speed instead of the Schrödinger equation used for traditional semiconductors [Castro Neto et al. 2009].

Figure 5.2: Sketch of the electronic structure of graphene, cone-shape linear electronic dispersion and density of states. Reprinted from ⁹.

5.3. Graphene applications

5.3.1. Introduction

The unique properties that graphene presents have motivated an intense work among physicists and engineers all around the world. Companies and research groups have been intensively working both in theoretical and experimental aspects to achieve the best graphene material and to experimentally introduce it into specific materials and applications with different target markets. Actually, the number of graphene suppliers from different synthesis methods (substrate-based CVD ~ 11 companies, direct exfoliation ~ 5, oxidation-reduction ~14...) is constantly increasing. Some of the graphene applications are nowadays ready for use (i.e., sport equipment, transparent conducting films (TCF)...), although most of them are still being investigated and could be industrialized in the next five to ten years (see *Table 5.1*).

Among all these new opportunities, regarding optoelectronic devices, we can list digital and radio frequency (RF) electronics, advanced sensors, transparent electronics, low-power switches, solar cells, LEDs, supercapacitors and battery energy storage (lithium-ion batteries with graphene electrodes) [Liu et al. 2012] .

⁹ www.ihip-microelectronics.com

Because of this big effort performed during the last decade, a huge number of patents in relation with graphene have been presented. Currently, Chinese organizations hold more patents than any other country, with Samsung leading with over 400 patents¹⁰.

Table 5.1: Applications timeline of graphene. Reprinted from¹⁰

5.3.2. Use of graphene in solar cells

Due to the exceptional properties that graphene exhibits, such as high electrical conductivity and high optical transparency among others, graphene is considered as a very interesting material for its incorporation as a transparent electrode in solar cells. This is why an intense activity has been carried out over the last years aiming its incorporation into different solar cells architectures.

For organic solar cells and LEDs, graphene has been proposed as an alternative to front contact of Indium Tin Oxide (ITO), which is quite expensive due to the increase in indium cost and because the optical transmittance of the ITO cuts off at the UV range while graphene does not [Jae-Phil et al. 2011]. Despite the good ITO sheet resistance (around 10-30 Ω/sq), a big work is being done with the purpose of reducing graphene sheet resistance. A graphene monolayer exhibits around 300-1000 Ω/sq [Jae-Phil et al. 2011]. One way to reduce the sheet resistance is by doping. A type of doping is the use of AuCl_3 (5-20mM) which has resulted in a value around 90 Ω/sq (p-doped graphene). The use of gold doped graphene in LEDs, has shown an

¹⁰ IDTechEx Research report: Graphene Markets, Technologies and Opportunities 2014-2024

improvement in electrical performance improvement and in the light output which was enhanced by about 20 % over the ITO LED [Cho et al. 2013]. However, although the expected doping effect is to reduce the graphene sheet resistance, it also has a deleterious impact on the optical transmittance in the visible range which could be reduced from 89% to 78% (with Au nanoparticles with an average diameter of $50\text{nm} \pm 20\text{nm}$).

Moreover, when graphene is in contact with semiconductors like GaAs, Si, GaN, carrier transfer takes place and rectification behavior occurs [Tongay et al. 2012]. Using graphene as a current spreading in InGaN p-i-n based solar cells has shown the same solar cell performance as the ones using ITO as an electrode with efficiencies of 1.2% [Jae-Phil et al. 2011]. Another example investigated is the graphene/Si junction which has resulted in efficiencies of 1.94-2.66% and up to 5.95% when using chemical doping treatments [Cui et al. 2013, Li et al. 2010, Tongay et al. 2012]. This has been also been studied for a bilayer of graphene/n-type GaAs substrate showing an open circuit voltage of 0.65V and a conversion efficiency of 1.95 % [Jie et al. 2013]. Moreover, theoretical calculations when optimizing several parameters as work function, number of graphene layers, antireflection coating, etc. have shown efficiencies of 11% [Lin et al. 2014].

In relation to the nanowires field, graphene has been also explored as a substrate for the growth of GaAs nanowires which are being proposed for high efficiency and low cost solar cells [Munshi et al. 2012]. In nanowires, strain due to lattice mismatch is a much smaller problem since the strain can be accommodated in the axial direction [Borgström et al. 2011]. This allows for a much larger freedom in combining materials which is more reduced in the bulk growth case due to the lattice matching requisite in some techniques. In the case of silicon nanowire arrays, graphene has been used to coat them to form graphene/silicon nanowires Schottky junction solar cells with efficiencies up to 2.86% [Fan et al. 2011].

Graphene has been also explored in dye-sensitized solar cells as an alternative metal-free electrocatalyst. Furthermore, doping graphene with nitrogen or boron has demonstrated to improve the catalytic reaction and thus, the solar cell performance to values of 6.73% in the case of boron doped graphene [Hou et al. 2013]. In addition, exploring the use of graphene as 2D bridges into the nanocrystalline electrodes of dye-sensitized solar cells, the electron transport is enhanced and the recombination is reduced showing an efficiency of ~7% [Yang et al. 2010].

In quantum dot solar cells, graphene could enhance the extraction of the photogenerated carriers [Guo et al. 2010, Zhu et al. 2014].

Additionally, a deep investigation is being done regarding the interaction of graphene with another 2D materials like transition metal dichalcogenides (MoS_2 , MoSe_2 ...). It has been demonstrated that photovoltaic devices based on MoS_2 /Graphene can provide conversion efficiencies up to 1% [Bernardi et al. 2013] .

In the aforementioned cases, graphene was used in low efficiency solar cells. So why not to use graphene in high efficiency solar cells? This is why, in 2012 we started to study the incorporation of graphene in III-V concentrator solar cells. Accordingly, this Chapter 5 and 6 are focused on the study of graphene for its incorporation in MJSC, and in particular on a lattice matched TJSC. During the development of this thesis, scarce work about the integration of graphene in MJSC has been published. The incorporation of graphene as an electrode for TJSCs was performed by Samsung. At 565 suns, the efficiency of the solar cells integrating graphene was around 19.6% while the same solar cell without graphene was 17.28% for the same concentration [Chang et al. 2013]. Another interesting work was found in relation to the use of graphene quantum dots on top of the active area of a MJSC which led to a conversion efficiency of 33.2%. [Lin et al. 2016].

Table 5.2: Summary of the efficiencies achieved till now for different solar cells integrating graphene

<i>Solar cell device</i>	<i>Efficiency achieved η (%)</i>
Graphene-Si junctions	1.94-2.66
Graphene doped- Si junctions	5.95
Graphene-GaAs junctions	1.95
Graphene-Si nanowires	2.86
Graphene as an electrode for InGaN p-i-n based solar cells	1.2
Graphene quantum dots in perovskite solar cells	10.15
Graphene on dye-sensitized solar cells	7
Graphene/ MoS_2	1
Graphene as an electrode for III-V multijunctions solar cells	19.6
III-V triple junction solar cells with graphene quantum dots	33.2

As it can be observed, graphene is considered as a good candidate to improve solar cells. It seems that it can be tuned and fitted according to the different needs of each solar cell approach. Table 5.2 summarizes the different solar cell applications that integrate graphene with the corresponding efficiency achieved. A lot of work is still ongoing to improve all these efficiencies.

5.3.3. Incorporation of graphene in III-V triple junction solar cells

III-V multijunction solar cells operating under concentrated light exhibit losses mainly because of the presence of lateral series resistances. A key component of these series resistances are those of the front metal grid and top emitter/window. Due to unique graphene electrical properties, its potential to be integrated on top of a multijunction solar cell makes it highly attractive. On the one hand, the idea of depositing graphene on top of the cell is mainly to demonstrate if graphene is able to extract vertically the photocurrent from the window and emitter layers, thus helping the lateral current flow to reach the front metal grid. On the other hand, graphene could also help in the photocurrent extraction by allowing an additional path in parallel to the front metal grid.

However, the electrical advantages of using graphene would be counterbalanced if graphene absorbs too much light. One single graphene layer is expected to absorb 2-3% of the impinging light. Though, since the refractive index of graphene is close to 3, it could constitute an antireflection coating together with the commonly used antireflecting systems such as ZnS ($n \sim 2.3$) and MgF_2 ($n \sim 1.4$). This antireflecting role of graphene could compensate partially its absorption.

For this purpose three main aspects must be accomplished:

- Graphene layer/s should have a sheet resistance between 200-500 Ω /sq.
- Graphene should be optically transparent with a transmittivity of 97-98%.
- A proper band bending between graphene and the top III-V window layer is needed in order to extract vertically the photocurrent.

All these requisites are going to be studied in Chapter 5 while the graphene incorporation in TJSC will be analyzed in Chapter 6. Since graphene properties are very dependent on its manufacturing process, in this chapter we will describe and characterize the graphene obtention processes we have followed in sections 5.4 and 5.5.

5.4. Synthesis of Graphene by Chemical Vapor Deposition (CVD).

5.4.1. Introduction

Different production methods yield graphene with different qualities, and are thus suited for different types of experiments and applications. In this section, the main types of synthesis are briefly mentioned showing the advantages and disadvantages of each one. Only graphene grown by Chemical Vapor Deposition (CVD) on a Cu substrate will be described in more detail since the graphene samples used along this Thesis have been synthesized by this method. Our choice was based in the very good optoelectronic properties together with the large area layers achieved by CVD which are key for photovoltaic applications.

5.4.2. Differences between various graphene synthesis methods

Since the discovery of 2D materials and specially graphene, several methods have been developed and are still being improved for the synthesis of graphene. Some of the most important methods used are: Exfoliation, Chemical Vapor Deposition (CVD), liquid phase and thermal exfoliation, synthesis on SiC substrates and molecular assembly.

Figure 5.3: Production methods of graphene in terms of quality and prize for any particular application. Reprinted from¹¹.

¹¹ K.S.Novoselov et al "A road map for Graphene" *Nature* 490,192-200. October (2012)

Graphene exfoliation based on the production of graphene flakes (tens of microns in size) by using a scotch tape, can be considered as the best quality graphene production method in terms of structural integrity (see *Figure 5.3*). However, the control of the number of exfoliated graphene flakes obtained can be difficult together with the very low yield achieved. On the other hand, liquid-phase exfoliation can introduce structural and electronic disorder in graphene [Paton et al. 2014]. Moreover, the production of arrays of novel materials such as graphene by molecular assembly has been also studied. In particular, an improvement between a graphene sheet random deposition versus a specific location and into a desired pattern has been achieved [Wang et al. 2009]. However, these routes cannot be used for the large scale production of graphene sheets.

For many applications such as micro and nano optoelectronics, the achievement of large area graphene free of defects and with high quality is required. Moreover, graphene synthesis can be accomplished by using a silicon carbide (SiC) substrate. One way is defined as SiC sublimation where the SiC substrate is converted into graphene via sublimation of silicon atoms when it is heated under vacuum at temperatures of $\sim 1400^{\circ}\text{C}$ [Bai et al. 2002, Charrier et al. 2002]. It is a high cost technique with typical SiC wafer size not higher than 4-inch, which is a disadvantage for its use in mass production. The other way of using SiC substrates to obtain graphene is by CVD where propane and argon with temperatures between $1500\text{--}1700^{\circ}\text{C}$ are used. On the other hand, epitaxial graphene on SiC is the only large area graphene that has unique azimuthal orientation [Avouris et al. 2012]. In contrast, the size production of CVD graphene on metal substrates has been increasing during the last years. In fact, Samsung developed 30-inch graphene sheet in 2011 [Bae et al. 2010]. One year later, in 2012, Sony has produced graphene sheets up to 100 meters in length and 23 cm in width by employing roll to roll methods which is the largest area graphene sheet in the world by far [Kobayashi et al. 2013]. One of the main limitations of CVD method is that a subsequent transfer process is required. This step includes the removal of the metallic substrate and the transfer of the graphene film onto the desired surfaces depending on the applications. In our particular case, graphene has to be transferred onto multijunction solar cells.

5.4.3. Chemical Vapor Deposition of graphene

The first report on CVD synthesis of few layers of graphene (FLG) was published in 2006 [Somani et al. 2006]. Since then, a lot of efforts and developments have been carried out with the final goal of producing a high quality and large area graphene [Li et al. 2009]. CVD graphene is known to be polycrystalline with domains sizes from micrometers to millimeters. The use of several transition metal substrates (Pd, Ni, Cu...) as the catalytic precursor has been widely explored. It has been found that Cu is an excellent candidate that can provide large areas of a

single layer graphene (95%) while the remaining graphene is 2-3 layers thick, independently of growth parameters like growth time, heating and cooling rates. This is because of the lower C solubility on Cu as compared to Ni, which was previously used (less than 0.001 atom% at 1000 °C versus 1.3 atom% at 1000 °C in pure Ni). The lower C solubility on Cu forces the graphene growth process to be performed at the surface (self-limiting) [Li et al. 2009]. Thus, in this self-limiting process, adsorption, decomposition and diffusion of molecules is carried out on the catalytic surface. On the contrary, in Ni foils, due to higher solubility of carbon, graphene growth occurs by carbon bulk diffusion and segregation during the cooling step.

Figure 5.4: a) Schematic image of the synthesis of graphene by CVD. Simple approach of CVD graphene by the use of a tubular furnace, a vacuum pump and a piece of a thin film of substrate (in this case copper foil of ~25μm). Precursors such as CH₄ and H₂ are injected at a typical temperature of 1000°C. Reprinted from MIT at Jing kong's group¹². b) Graphene growth steps by CVD.

Figure 5.4 a) shows the CVD growth of graphene at research scale. Graphene growth was performed during the PhD stage of Laura Barrutia at MIT at Tomas Palacios's group (from April to July 2015). Graphene was grown following the recipes of the MIT's group [Fang et al.]. Graphene was grown on copper foils (~ 25μ thick, 99.9%) at temperatures up to 1000°C in a conventional furnace using a mixture of methane (CH₄) and hydrogen (H₂) as precursor gases. Copper (Cu) foils of ~ 2.5 x10 cm were pretreated by dipping it into a Cu etchant (nitric acid) during 30s followed by rinsing into deionized water (DI) and drying with nitrogen (N₂). This step reduces possible native oxides on the Cu foil that could affect graphene growth [Kim et al. 2013]. Then, the Cu foil is carefully placed at the center of the heating zone inside the quartz tube (see Figure 5.4a). Graphene growth takes place on both sides of the Cu foil. The graphene growth steps are represented in Figure 5.4 b. Once the desired temperature was achieved, the copper foil was first annealed. High-temperature treatments of the substrate revealed to be helpful for the reduction of volatile impurities, contaminants, and defects on the copper surface, that strongly affect graphene nucleation [Muñoz et al. 2013]. Moreover, this annealing treatment helps reduce

¹² <http://www.rle.mit.edu/nmeg/>

its roughness and increase the grain size from a few micrometers to $\sim 100 \mu\text{m}$, since it was found that copper foils with larger grain size yield higher-quality graphene films, as suggested by [Li et al. 2009].

One important aspect is the polycrystalline structure of graphene. Most of the metals where graphene is grown are polycrystalline, although the hexagonal lattice of Cu(111) favors the high quality of as grown graphene [Li et al. 2009]. Additionally, even if graphene is grown on a single crystal Cu, it still has a multidomain structure, because of the rotational disorder between domains and the many grain boundaries. The result is a graphene layer within single crystal domains azimuthally rotated relative to neighboring domains and stitched together with defective domain boundaries, such as alternating pentagon-heptagon structures see (Figure 5.5).

Figure 5.5: Schematic of main steps that take place during the CVD graphene. A) Copper foil of $25\text{-}30\mu\text{m}$ of thickness with a native oxide layer on top of it. B) Surface deoxidation by a thermal treatment. C) Nucleation of graphene islands under a CH_4/H_2 atmosphere. D) Graphene surface coverage with different in-plane orientations. Reprinted from [Zaretski et al. 2015] .

Furthermore, due to the thermal expansion coefficient difference between Cu and graphene, wrinkles are formed during the cooling step. Moreover, in other works [Li et al. 2009] wrinkles have been found to cross Cu grain boundaries, indicating that the graphene film is continuous. Small flakes are also evident in the optical image showing the presence of small 2MLG graphene sheets (Figure 5.6).

To end up with this first introduction of our CVD graphene, Figure 5.7 shows a TEM image with the characteristic hexagonal lattice structure of the graphene monolayer along. As graphene monolayers are typically synthesized in polycrystalline Cu foils, the resulting graphene monolayers are polycrystalline with many single-crystalline grains (of $10\text{-}20$ microns) with different orientations with each other and separated by grain boundaries. Additionally, graphene grains can cross Cu grain boundaries [Yu et al. 2011]

Figure 5.6: Optical Microscope image of 1MLG grown by CVD on a Cu substrate and transferred into a SiO₂/Si substrate (optical magnification x100). Small flakes and wrinkles during the cooling step can be appreciated.

Figure 5.7: High resolution TEM images of a CVD graphene monolayer.

5.5. Wet transfer method of CVD-grown graphene

5.5.1. Introduction

As it was already mentioned in the previous section, CVD graphene synthesis seems to be one of the most promising alternatives to be used for mass production. Not only large area of uniform graphene is achieved but it has been also demonstrated that CVD graphene grown on catalytic metals is of high enough quality for optoelectronic devices where transparency and conductivity play an important role [Li et al. 2009] .

Despite this promising synthesis method, subsequent graphene transfer into a desired substrate is required. As of today, graphene growth on insulators is not yet available. That is why graphene transfer onto a substrate of interest (insulator, transparent...) for its final application can be defined as a must to combine with this synthesis technique.

One of the most common procedures to do the graphene transfer is the so-called “wet transfer” method [Reina et al. 2009]. In this method, a polymer film is deposited on top of the graphene and after that the catalyst metal is etched away. At the same time, the inconvenient of using this method, is that the resulting graphene has been exposed to the metal etchant, polymer residues and dust particles that could be adhered during the different transferring steps and could strongly affect the final properties of graphene.

Other alternatives have been widely studied. Each technique differs from the others but all share a common goal: to enhance and preserve graphene properties. Some of the different techniques being studied are the so-called “bubble transfer”, roll to roll (R2R) method and the free transfer.

Regarding the bubble transfer technique proposed by Cheng et al [Gao et al. 2012], it is based on the mechanical separation of graphene from the metal substrate by electrochemical delamination. Graphene on Cu is covered by poly (methyl methacrylate) PMMA and inserted as the cathode electrode in an aqueous solution. By applying a voltage, H₂ bubbles form at the cathode of the electrolytic cell and emerge at the graphene/metal interface. The two main advantages of this transfer process are: a) the two graphene layers that grow at both sides of the metal substrate can be transferred and b) the substrate is not chemically etched. An intensive work has been done regarding the application of this process, in particularly for Cu [Wang et al. 2011].

On the contrary, for the dry etching techniques, poly (dimethylsiloxane) (PMDS) and thermal release tape (TRT) can be used to substitute polymers (i.e PMMA) such as in the so-called the roll to roll method (R2R). In this process, the metal substrate (i.e. Cu) is also chemically etched. The big advantage of the R2R method is that it enables the transference into flexible target substrates by inserting both the graphene and the flat or curved substrate between the two rollers at a temperature of 90-120°C [Bae et al. 2010]. Unfortunately, R2R also contaminates the transferred graphene surface with the adhesive from the thermal release tape and may induce a mechanical stress that could damage graphene when rigid target substrates are used such as semiconductor wafers. In this case, other dry methods based on hot pressure [Kang et al. 2012] or low temperature [Cha et al. 2015, Suk et al. 2011] are being proposed as alternatives.

Finally, it is worth mentioning the fast evolution of the free-transfer methods regarding the preparation of target substrates to directly grow graphene on them such as Cu/Ni on SiO₂/Si substrates [Ismach et al. 2010, Levendorf et al. 2009], Cu deposited on insulating substrates [Kapas et al. 2016, Su et al. 2011], flexible plastic surface [Yong-Jin et al. 2012] or even the direct growth of graphene on CMOS compatible Ge/Si(001) surfaces [Dabrowski et al. 2016, Wang et al. 2013].

As a key aspect to take into account is that different graphene transfer methods involve different graphene final properties [Chen et al. 2011]. In our particular case, the conventional wet transfer process has been chosen as the transfer technique for CVD graphene onto our solar cells. The reasons for that choice are: a) some graphene samples used in this Thesis have been provided by a company (Graphenea) who uses both CVD graphene growth and wet transfer; b) the know-how of the wet transfer process has been also acquired during the stay of Laura Barrutia at MIT with the subsequent know-how transfer to IES-UPM. Nevertheless, all this work has been done being conscious of the advantages and disadvantages that the wet transfer involves, for the two aforementioned reasons, a comparison between the wet transfer process at MIT and IES is possible.

5.5.2. The IES-UPM graphene transfer process

As it has been already mentioned in the last section (5.5.1), after CVD growth, graphene needs to be transferred to a specific substrate which directly depends on the target application. In our particular case, CVD graphene has been transferred to different substrates such as SiO₂/Si substrates, semiconductor samples, solar cells or glass substrates. What is common for all these graphene transfers is the way graphene has been transferred, namely by a conventional wet transfer process. As it is already known, by using this method, the graphene layer could be

damaged or end up unintentionally with a higher doping level due to several agents present at the different steps (such as Cu etchant, dust particles, water molecules or PMMA residues) degrading its final electronic mobility [Capasso et al. 2014, Leclercq. J et al. 2016] or changing its optical properties [Ochoa-Martinez et al. 2015]. Moreover, previous reports indicate that not only PMMA can be a p-type dopant on graphene [Chen et al. 2007, Na et al. 2006] but it has been also reported that the presence of oxygen may also influence the p-type doping level [Ryu et al. 2010]. Additionally, wet transfer processes must be done with the best cleaning conditions in order to avoid further contamination at the graphene/substrate interface. Another important aspect of using this method is the maximum transferrable size which is actually limited to less than a few inches because of the weak mechanical strength of spin-coated PMMA layers. Fortunately, this size is large enough for the purposes of this Thesis.

The wet transfer method developed at MIT and later established at IES-UPM can be divided into different steps. It is worth mentioning one more time, that each step is crucial when working with graphene. Moreover, graphene handling between each step may induce cracks or tears [Li et al. 2009]. The transparency of the PMMA/graphene stack and its manipulation from one glass beaker to another with the help of a glass holder, makes the process difficult so sometimes graphene was bent or broken, since more than 6 times, graphene is manipulated from one glass beaker to another along the steps.

5.5.3. Process description

CVD graphene on Cu with typical sizes of $1 \times 1 \text{ cm}^2$ is coated with a layer of poly methyl methacrylate (PMMA, 950 A9, MicroChem, diluted to 4.5% in anisole) at 2500 rpm for 1 min (~200nm of thickness). After coating, the sample is placed in an oven at 130 °C for 10-15 min. Then, the Cu is chemically etched by floating the coated sample on the ferric chloride solution (CE-100, Transene Company Inc.) for 30min. During this time, the Cu foil starts to be etched at the corners and after some minutes (10-20min) samples turns into a transparent layer formed by a free standing PMMA/graphene stack. 30 min has been determined as the typical etching time since a shorter time is not enough to etch the copper completely while longer than 30 min will not improve it. Nevertheless, some Cu spots that would need some extra time is sometimes observed. Subsequently, we wash the PMMA/graphene on three water steps and rinse it in HCl:H₂O (1:3) for 5 min. These steps help remove some debris from the Cu etchant such as oxidized metal particles. The sample is rinsed again in another three water steps before it is transferred to the desired substrate. Drying consciously with N₂ helps remove water at the interface (graphene/substrate). For a better result, two heating steps (heating #1 during 15min at 80°C and heating #2

during 15min at 120°C) are done in an oven to further reduce the amount of water molecules and improve PMMA/graphene adherence to the substrate. After the heating steps, PMMA is partially removed by acetone (≥ 2 h) and isopropanol or methanol. Therefore, thermal treatments help remove PMMA and clean the graphene surface leaving it almost free of PMMA although some particles may persist [Pirkle et al. 2011]. In our particular case, 2h-3h of thermal annealing at 350°C under ~ 200 sccm H_2 or under ~ 200 sccm of H_2 and ~ 200 sccm of Ar ~ 200 sccm could be defined as the typical range. For a better understanding, *Figure 5.8* summarizes this wet transfer method.

Figure 5.8: Flow diagram of the different wet transfer steps for the graphene transfer to a substrate of interest (SOI) carried out at IES-UPM.

It should be mentioned, that the transfer process carried out at IES-UPM has been done with CVD graphene samples grown by a company (Graphenea), thus the deposition of a PMMA layer to protect graphene was done by this company prior to delivering us the samples. Moreover, some of the graphene samples studied along this document have been grown and transferred completely by that company. Finally, for graphene samples grown at MIT, the full process (from the initial growth and preparation of the Cu foil to the final graphene transfer to a desired substrate) were done during the MIT stay in this Thesis.

As an example, *Table 5.3* compares some graphene sheet resistances obtained for one graphene monolayer (1MLG) and two graphene monolayers (2MLG) that had been grown in Graphenea but transferred by the wet transfer method at two different places (at Graphenea and at IES-UPM). As can be observed, graphene sheet resistance and thus its resistivity is preserved quite similar in all circumstances which confirms the satisfactory transfer at IES-UPM. It is also interesting to mention how the sheet resistance is half when 2MLG are transferred. More details about graphene sheet resistance and its resistivity will be explained in section 5.6 (Graphene Characterization).

Table 5.3: Comparison of graphene sheet resistances of 1-2MLG grown by CVD and transferred by the wet transfer method at different places.

<i>CVD growth</i>	<i>Wet transfer</i>	<i>Graphene monolayers</i>	<i>R_{sheet} (Ω/sq)</i>
<i>By Graphenea</i>	Graphenea	2MLG	~ 214
<i>By Graphenea</i>	Graphenea	1MLG	~ 418
<i>By Graphenea</i>	Transfer 1_IES	1MLG	~ 453
<i>By Graphenea</i>	Transfer 2_IES	2MLG	~ 213

5.5.4. Process characterization

To complete the graphene transfer process by the wet transfer method, Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) was used in order to determine the purity and structure after graphene was transferred onto a desired substrate. For this purpose, different CVD graphene samples were studied. ARXPS was carried out on as-grown graphene on copper foils, on graphene transferred onto a native SiO₂/Si substrate and also on graphene transferred onto a thermal oxide SiO₂ $\sim 300nm$ /Si substrate. ARXPS measurements were performed at the Nanotech Unit in Malaga University. A Thermo Scientific Multilab 2000 spectrometer was used, fitted with a dual anode (Mg-K α , Al-K α) X-ray source and a 110 mm mean radius hemispherical sector analyzer. With the aim of exploring the evolution of the surface composition on top of and under the graphene layer, measurements were made at three different take-off angles (10°, 45° and 90°, outing photoelectrons pathway measured from the sample surface), changing thus the explored depth. Further information and details on ARXPS measurements can be obtained in [Ochoa-Martinez et al. 2015].

For as-grown graphene on copper foils, ARXPS measurements reveal a clean surface with no traces of neither oxygen nor any other contaminant on top of the graphene. However, as the explored depth increases (45° and 90°) a small signature from O-C bonds appears both in the C1s and O1s core level signals. Both facts strongly suggest that the top surface of the as grown

graphene layer is free from contaminants, which would be a proof of its quality, although there is some oxygen trapped under the graphene layer.

On the other hand, transferred graphene layers onto native SiO_2/Si substrates (MLG sample) show the presence of transfer debris on top of the graphene surface. This is a proof of the presence of carbons atoms linked to the oxygen on top of the graphene surface. Thus, after the transfer process, graphene layers seem to be sandwiched between two contamination layers. It should be taken into account that CVD graphene layers on Cu are not perfectly flat [Li et al. 2009] and this fact would favor the appearance of these residual layers.

Finally, *Figure 5.9* shows an example of the study of C1s and O1s core levels performed on samples of monolayer graphene transferred onto thermal SiO_2/Si (MLG-TO sample). In this case, there is a higher presence of C-O, C=O and O-C=O bonds suggesting PMMA polymer debris on top of the graphene layer contributing both to C1s and O1s core level signals (see *Figure 5.9*). About 15% of the C1s signal at the lowest take-off angle is due to this precursor debris. Their intensity strongly diminishes with explored depth, which indicates that its presence is restricted to a contamination layer on top of the graphene.

Figure 5.9: Example of a deconvolution of C1s (left) and O1s (right) core level signals in their constituents, for a CVD graphene layer transferred to a thermal oxide SiO_2/Si substrate (so-called MLG on TO sample). Take-off angle, and therefore explored depth, increase from top to bottom [Ochoa-Martinez et al. 2015].

As it has been presented in this section and according to the literature [Pirkle et al. 2011], ARXPS reveals the presence of dust particles such as PMMA residues, water molecules and

oxygen that could be stacked on top or underneath graphene layers. Since graphene properties are affected by such contamination, it could be stated that graphene properties depend directly on both the synthesis mechanism and the transfer method that has been chosen. Moreover, the characteristics of the PMMA deposition on top of the graphene (spin coating and concentration) are crucial since higher PMMA concentrations leave more PMMA residues that may increase the amount of H_2O/O_2 being adsorbed [Borin Barin et al. 2015, Suk et al. 2011].

5.5.5. Transfer of more than one monolayer graphene

In order to achieve an enhanced lateral conductivity of graphene, the idea of transferring more than one graphene monolayer has been also considered. With that purpose, one could think that growing more than one monolayer graphene (i.e...2MLG, 3ML) could be a fast or better option rather than transferring them. The interesting result, is that 2MLG grown by CVD, presents different properties than the layer by layer transfer of 2MLG, on top of the other. Actually a bilayer graphene has a tunable gap of up to about 250meV [Zhang et al. 2009]. The stacking order and coupling in few-layer graphene were demonstrated to affect the electrical properties of the material [Lopes dos Santos et al. 2007, Mak et al. 2010]. On the contrary, a process of layer-by-layer transfer could not produce AB (Bernal) stacked graphene due to the random orientation between the transferred layers [Liu et al. 2014, Sun et al. 2016, Yan et al. 2011]. *Figure 5.10.b* represents the AB Bernal stack, where “A” atoms of the top layer are located atop the “B” atoms from the layer underneath.

Figure 5.10: Sketch of the hexagonal honeycomb of 1MLG based on two carbon sublattices. A) The carbon atoms in the A and B sublattices are colored in blue and yellow, respectively. B) Schematic of the Bernal or AB stacked bilayer graphene. Please notice that no random orientation is presented. Reprinted from [Gao 2014] .

Accordingly, the transfer of 2MLG by layer-by-layer transfer normally involves non-AB stacked planes, which means that the graphene layers are rotated several grades to each other and what we have is actually one monolayer on top of another monolayer with the promising properties of graphene. The big disadvantage, is the amount of dust particles already described

for 1MLG transfer, that may be even higher for 2MLG. This is because the wet transfer method described in Section 5.5 will be repeated as the number of required layers is increased.

Figure 5.11 Optical Microscope images of 1MLG (left) and 2MLG (right) grown by CVD on a Cu substrate and transferred into a SiO₂/Si substrate (optical magnification x100).

Figure 5.12: Deconvolution of C1s (left) and O1s 45° (right) core level signals in their constituents, for two CVD graphene monolayers (BLG or 2MLG) transferred one on top of each other to a native SiO₂/Si substrate (so-called BLG sample). Take-off angle, and therefore explored depth, increase from top to bottom [Ochoa-Martinez et al. 2015].

In relation with the ARXPS measurements, for bilayer graphene sample (BLG), PMMA debris are again clearly identified among the constituents of the C1s core level signal. As it is evident in Figure 5.12, contributions from CO, C=O and O-C=O bonds can be resolved [Baraket et al. 2010].

For this sample, they can be easily detected at 45° and 90° take-off angles, and the C-O signal increases in intensity with explored depth, which is indicative of its presence in an intermediate contamination layer between the two graphene sheets. Therefore, the ARXPS analysis suggests the need to include additional layers beneath and on top of the transferred graphene layers in order to better describe the real stacked structures.

To summarize, ARXPS provides information and reveals the real stack that is formed when one monolayer graphene (MLG) or two monolayers of graphene (BLG) are transferred by the wet transfer method. As the number of graphene layers is increased, the layer-by layer method is linearly increased and thus, the amount of effective medium approximation (EMA) interlayers (see *Figure 5.13* for a bilayer graphene).

Figure 5.13: Sketch of the layer structure of MLG and BLG transferred on a native $\text{SiO}_2 \sim 3\text{nm}/\text{Si}$ substrate determined by ARXPS.

Summarizing, in this section we have presented one of the most commonly used methods for transferring graphene, the wet transfer method. This method has been established during this Thesis for the first time at IES-UPM. However this PMMA-based transfer process still presents challenges in yielding a clean and high quality graphene.

At the same time, ARXPS was used to determine the real stacked structure after graphene was transferred onto a desired substrate. What was observed, is that graphene transfer is directly influenced not only by the different steps of the wet transfer method, but also by the substrate used. Moreover, the presence of water molecules, oxygen at the interface of graphene and the substrate together with PMMA residues are drastically reduced when thermal annealing treatments are carried out [Ochoa-Martinez et al. 2015]. Unfortunately, after such treatments the presence of some of this debris is unavoidable and thus the influence on the electrical properties of graphene (mobility, doping, work function...). That is why is so important to carefully characterize the optical and electrical properties of our CVD graphene, since the final purpose is the integration of it on a MJSC structure.

Considering some of the disadvantages of this method, it is important to mention very interesting works in relation to the reduction of possible cracks that may be produced during the PMMA removal. This is mainly due to possible gaps that may exist between graphene and the substrate. In order to make a better contact of graphene with the substrate of interest, Li et al proposed the deposition of a second PMMA layer [Li et al. 2009]. Moreover, the impact of the PMMA baking time and temperature has been also considered [Borin Barin et al. 2015] as well as modified RCA cleaning processes that could help to avoid cracks formation and degradation of graphene quality [Liang et al. 2011]. On this line, a very interesting work when more than one graphene monolayer wants to be deposited has been suggested. It consist on the transfer of one monolayer graphene directly on top of another graphene monolayer/Cu foil. In this case only PMMA is deposited on top of one of the monolayers and another monolayer graphene on copper foil is used to fish out the graphene/PMMA film from deionized water. Due the face-to-face superposition of graphene layers of the sides with clean surface, there is no PMMA between the graphene layers reducing considerably the presence of these residues [Chen et al. 2014]. Las but not least, a very interesting work regarding graphene wet transfer process has been developed by [Boscá et al. 2016]. It is based on an automatic process in which different wet transfer steps (Cu etching, water steps, drying...) do not require the aforementioned handling skill so graphene quality is improved and preserved.

5.5.6. Detachment of graphene

As previously pointed out, graphene is just a one-atom thick layer, and this fact makes graphene very sensitive and interactive with the surroundings such as the substrate where it is transferred to. Regarding this sensitivity, one problem that frequently arises is the graphene detachment. Graphene detachment is defined as the peel off and roll up of graphene that could occur during punctual processing steps. The origin of detachment is the lack of a good and uniform adhesion of graphene to the substrate. It must be pointed out that Cu foil where graphene monolayers are grown, is not atomically flat but it has a roughness of $\sim 100\text{nm}$. After the PMMA coverage on top of graphene and the subsequent transfer, graphene could be damaged and also partially adhered to the substrate of interest. Moreover, humidity levels higher than 45% during processing could affect graphene in a detrimental way.

During the development of this Thesis, several samples were supplied by Graphenea. These graphene samples consisted in a monolayer of CVD graphene transferred by the wet transfer method into a thermal oxide $\text{SiO}_2 \sim 300\text{nm}$ /Si substrate. These samples had been received and processed in different periods. Both in the company and in this thesis, different procedures were changed in order to improve in general aspects the graphene transfer and to solve the graphene

detachment. In some of the graphene batches, high detachment was detected. This detachment was mainly present in two specific steps during the processing of TLM patterns that will be described section 5.6.4 (electrical characterization). With the idea of processing TLM pads on a graphene/SiO₂ sample, typical processing steps (photolithography, metal evaporation, liftoff...) are required. One of the critical steps was the optical lithography. Ultraviolet Light (UVL) photolithography is used to define the TLM patterns, depending on the mask, negative or positive photoresist is used. After the exposure to UVL, the sample is rinsed in a developer for some seconds and later on in ionized water and dried with pure nitrogen (N₂). Graphene detachment was just identified after the developer step. This detachment was severe in some of the samples and lighter in others. *Figure 5.14a* shows an example of a light graphene detachment in some of the TLM pads.

Figure 5.14: a) Optical image of graphene detachment present in some TLM patterns after the developer step during the photolithography processing. b.1) Optical microscope image of graphene definition patterns by RIE. No detachment of graphene is observed. Pink pads correspond to SiO₂ areas where graphene has been etched away intentionally by RIE technique. Grey pads correspond to graphene pads not etched by RIE. b.2) Optical microscope image of the definition of the TLM pads in between of graphene and SiO₂ by photolithography step. No detachment of graphene is observed after the photoresist, UVL, developer and water step. b.3) Graphene detachment during the liftoff process. Both graphene and metal had been peeled off leaving the SiO₂ under them. This image shows that the metallization is preserved on the SiO₂ area revealing that adhesion of the metal is good. c) Optical image of high quality graphene TLMs. No detachment is observed along the different photolithography, metallization and liftoff steps which indicates that thermal annealing prior processing is decisive.

Regarding this photolithography step, deposition of a few nanometers of (2-3 nm) of Al_2O_3 prior to the deposition of the photoresist step could be used to protect graphene from further contamination with photoresist dust particles [Hsu et al. 2011] . In this way, graphene will never be in contact with the photoresist. Moreover Al_2O_3 is etched away during the developer step since it contains dilute tetra-methyl ammonium hydroxide (TMAH) which is highly selective etchant for Al_2O_3 , so the oxide covering the developed region of the photoresist will be dissolved away and the graphene can be contacted with a metal. With that purpose, a very thin Al layer was deposited by thermal evaporation in some of the samples ($\sim 3\text{nm}$), after some minutes in atmosphere this thin layer was oxidized. Unfortunately, once more time after repeating the photolithography step, graphene detachment was also present. Additionally, it has been also found that developers with TMAH could affect graphene negatively. Our study was performed by using both positive and negative photoresist with the corresponding developers. Moreover, in order to discard the negative effect of our developers another graphene sample from a different company was processed in the same way. This time, no graphene detachment was observed, what it confirms that the developers and photoresist used were not the main agent responsible for the detachment observed. Moreover, the possible influence of the roughness of the SiO_2/Si substrate or the Cu foil could be the fact affecting graphene negatively.

Furthermore, the second step where detachment of graphene was observed, was during the liftoff step. After evaporation of the metal contacts, a liftoff step is done in order to remove both the photoresist and the metallization on top of this resist from non-desired areas. This is done by dipping the sample in acetone for some minutes. What it was observed after this step, was that the metallization has been also removed from the TLM graphene pads. On a first approach, it was thought that adhesion between graphene and the metal contacts was not good enough. But this assumption was discarded since optical microscope images (*Figure 5.14c*) show that graphene has been also detached together with the metallization revealing the pink area related to the SiO_2 layer that was below graphene. As of today, we can't confirm the main agent responsible for graphene detachment, but what it has been observed, is that detachment of graphene is highly reduced after thermal treatments in a N_2 atmosphere at least at 120°C - 300°C for 30 min. Graphene/ SiO_2/Si samples that are received from Graphenea company had been transferred at least weeks in advance. As a result, annealing the samples just prior to photolithography step will remove possible water molecules that had been adsorbed and adhesion will be reinforced, reducing the possibility of detachment during the processing. *Figure 5.14 c* shows an example of a final graphene TLM pads with a satisfactory result.

5.6. Graphene characterization

5.6.1. Introduction

As it has been presented in the previous sections of this chapter, graphene synthesis technique together with the transferred method play an important role. With the aim of determine such graphene properties of our CVD graphene, both electrical and optical characterization were addressed. Several techniques have been used in order to know if this type of graphene could be integrated in our solar cells.

5.6.2. Work function of graphene

In this section, graphene's work function (Φ_G) has been obtained by Ultraviolet Photoelectron Spectroscopy (UPS) with an ionization source of He I (21.21eV) at the University of Malaga. The work function is a fundamental electronic property of any material, and provides understanding of the relative position of the Fermi surface levels since it determines the band alignment in the contact at the heterojunction to allow selective electron and hole transport. The work function of graphene is similar to that of graphite, ~ 4.6 eV [Takahashi et al. 1985], and depends on the number of layers [Lin et al. 2013].

Table 5.4: Summary of Graphene's work function gathering of the substrate

<i>Samples</i>	Φ_G (eV)
<i>CVD graphene directly grown on Cu</i>	~ 4.7
<i>CVD graphene transferred onto a Cu substrate</i>	~ 4.8
<i>CVD graphene transferred onto a native SiO₂ (3nm)/SiO substrate</i>	~ 5.0
<i>CVD graphene transferred onto a SiO₂ (300nm)/SiO substrate</i>	~ 5.6

In order to obtain information of the work function of our CVD graphene, several samples on different substrates (graphene directly grown on a copper foil, graphene transfer into a Cu or SiO₂/SiO substrates) were analyzed. Such characterization shows that the work function of graphene is highly dependent on the substrate. In our particular study Φ_G varies from ~ 4.7 eV for graphene directly grown on a copper foil up to 5.6 eV for graphene transferred on a 300 nm thermal growth SiO₂/Si substrate. However, when the SiO₂ is reduced to only a few nanometers (native oxide), Φ_G decreases ~ 0.6 eV. These results are consistent with the ARXPS analysis (section 5.5.4) performed on these kind of samples, where the amount of water molecules or PMMA residues was lower for the graphene grown directly on a Cu foil (without any transfer step) and higher for a graphene monolayer transferred onto a SiO₂/Si substrate affecting strongly

the amount of stack residues on intentionally grown thermal oxide SiO₂ of ~300nm rather than in a native SiO₂.

With all these results, the study of graphene's work function once it has been transferred onto a MJSC is of extreme interest. This important parameter will give us information about the electronic transport at the interface between graphene and the AlInP window layer and between graphene and the front contact metallization (AuGe/Ni/Au). Since the graphene/AlInP window interface is different from the graphene/metal interface, differences in the graphene work function are expected.

At the same time, the work function could be also affected by the surface state so, contamination or oxidation may have a significant influence. That is why pre-cleaning treatments in Argon (Ar) were performed for some of the samples to see this influence. This cleaning step is based on a sputtering step with argon ions during 60 seconds. The applied energy was ~ 3keV for surfaces without graphene coverage while a lower energy of ~1keV was applied for a surface with the presence of graphene (for the graphene/AlInP surface) in order to avoid graphene damage.

Moreover, the work function of the AuGe/Ni/Au metallization was also analyzed and used for the calibration for the subsequent measurements. *Figure 5.15* shows the binding energy diagram of this metallization which is the standard used in our TJSCs. The work function obtained for this metallization resulted in a value of ~5.05eV which is in the typical range of a gold sample. This was expected since the top material at the surface of this front metallization is based on hundred nanometers of gold.

Figure 5.15: UP-spectrum of the AuGe/Ni/Au sample analyzed for the calibration and subsequent measurement of the work function of the graphene/AlInP and graphene/AuGe/Ni/Au interfaces.

Table 5.5 summarizes the experimental graphene work function on top of the aforementioned AuGe/Ni/Au metallization and also on top of the AlInP window layer (this last one with and without thermal treatment). For graphene on top of an AlInP window surface, it can be observed how the value was slightly varied by using the pre-cleaning treatments. Since we are not sure about the impact of this pre-cleaning sputtering on graphene quality, both values will be considered in Chapter 6 for the study of the graphene/AlInP interface.

Table 5.5: Experimental work function measured by UPS

Samples	Φ_G (eV) with argon pre-cleaning	Φ_G (eV) without cleaning
Graphene/AuGe/Ni/Au	—	~ 4.98
Graphene /AlInP	~4.95	~ 4.86

Additionally, graphene work function and the ability to engineer it, is a very important factor governing the graphene's applications. Currently, graphene work function can be modulated by applying an electric field [Yu et al. 2009], by means of chemical doping [Jeong et al. 2010, Shi et al. 2010, Yi et al. 2011] and even by irradiation-induced defects [Chang et al. 2013]. Intentional doping graphene with the aim of modifying its work function will be presented in section 5.6.4.3.1.

5.6.3. Raman characterization: quality and number of layers

Following with the graphene characterization, Raman spectroscopy is performed on our CVD graphene samples. It is a non-destructive technique that has been extensively used to identify both number of layers and graphene quality [Ferrari et al. 2006, Graf et al. 2007].

Raman measurements were performed with a Raman Confocal Microscope (Horiba Jobin Yvon LabRam) during the Phd stage at MIT. The energy of the laser used for the excitation was 532nm with a beam diameter of $\sim 1\mu\text{m}$ and a power of 0.95mW to minimize the laser induced heating effect. By using Raman spectroscopy, interactions with molecular vibrations and phonons are studied. Looking at the Raman spectra (*Figure 5.16 a*) it can be identified two main peaks related to the primary in plane vibrational mode (the G band) which corresponds to the optical mode vibration of two neighboring carbon atoms on a graphene layer, and a second order two phonon process (the 2D band). These peaks are characteristic of graphene Raman feature and use to appear near $\sim 1580\text{ cm}^{-1}$ and $\sim 2680\text{ cm}^{-1}$, respectively. By calculating the intensity ratio between Raman 2D and G-bands, the number of active graphene layers is usually determined. A ratio of $I_{2D}/I_G \sim 2$ is normally obtained for one graphene monolayer. From *Figure 5.16* we can observed that this behavior is not confirmed in our particular case where the intensity of the 2D band is

lower than G band. In addition, the intensity ratio I_{2D}/I_G is also strongly dependent on the doping level. This fact could explain the low intensity obtained for the 2D band since 2D mode is much stronger affected by the doping level [Farmer et al. 2009]. At the same time, Raman spectra is also sensitive to the influence of the substrate where graphene layer is deposited [Huang et al. 2014]. Looking at *Figure 5.16*, there is a strong variation between the relative intensity of 2D and G peaks and the G peak position. For high doping levels (G peak above $\sim 1592\text{cm}^{-1}$) the ratio I_{2D}/I_G goes down to ~ 1 . According to [Das et al. 2008], it is actually suggested that the intensity ratio I_{2D}/I_G should not be used to estimate the number of graphene layers as contrary to other authors founded in literature [Graf et al. 2007, Gupta et al. 2006]. The most effective way to identify a single layer is by the shape of the 2D peak. Moreover, the full width at half maximum (FWHM) of the 2D band for the CVD graphene samples studied in this Thesis is around 31-35 cm^{-1} (Table 5.6) which is consistent with the value reported for graphene monolayers [Kim et al. 2015]. At the same time, the sharp and symmetric 2D band (see *Figure 5.17*) is used to identify graphene monolayer (MLG) [Ferrari et al. 2006].

Additionally, another peak may appear at $\sim 1355.12\text{ cm}^{-1}$. This is the D band peak and it is related to the presence of some defects. Only for one of the samples fabricated, D peak could be slightly appreciated (Raman spectrum for graphene sample G5) confirming that our graphene samples exhibit a high quality. *Figure 5.16* summarizes the Raman spectra obtained for our CVD graphene samples.

Figure 5.16: Raman spectra of CVD graphene samples (G5, Gc, G4 and G6) transferred by means of the wet transfer method.

Figure 5.17: Gaussian fitting of 2D Raman peak of CVD graphene. Accordingly, this symmetric 2D band reveals a single layer graphene

Table 5.6: Summary of the main peaks obtained in the Raman spectrum of different CVD graphene samples. The full width at half maximum (FWHM) of 2D band is also summarized.

Samples	2D band (cm ⁻¹)	FWHM (2D) (cm ⁻¹)	G Band (cm ⁻¹)	FWHM (G) (cm ⁻¹)
Gc	2688.39	31.2	1595.65	9.52
G4	2690.92	33.9	1601.81	11.32
G5	2687.66	35.4	1592.14	17.79
G6	2697.10	34.8	1605.86	10.31

From this Raman characterization, it can be concluded that the determination of the number of graphene layers is not so evident. Two main characteristic peaks (G and 2D) appear in the Raman spectra of our CVD graphene samples. The sharp and symmetric 2D peak confirms a single layer graphene although a low I_{2D}/I_G ratio is obtained. Therefore, I_{2D}/I_G ratio and peak position can be related to the final doping of the graphene layer which is influenced by the substrate effect and residues during the transfer process. At the same time, a lower I_{2D}/I_G ratio is related to a larger amount of charge impurities in graphene.

To end up with this Raman characterization, and following with the impact that thermal treatments could have on the graphene properties, a simple thermal treatment at 100°C for 20 min suggests a cleaner surface with a lower contamination possibly from water molecules adsorption (higher intensity of the main peaks Figure 5.18). Table 5.7 summarizes the positioning and the FWHM of the main peaks. As expected, a slight change in the positioning of the peaks to lower wavenumbers is obtained after the treatment.

Figure 5.18: Raman spectra of two different CVD graphene samples (G1 and G2) prior (red lines) and after (black lines) a heat treatment at 100°C for 20 min. The intensity of both G and 2D peaks is enhanced after the thermal treatment suggesting a cleaner surface and the evaporation of possible water residues. Raman spectra of Figure 5.18 were carried out at Malaga's University.

Table 5.7: Summary of the main peaks positions (2D and G) and their full width at half maximum (FWHM) obtained in the Raman spectrum of different CVD graphene samples prior and after the thermal treatment.

Prior to thermal annealing			After thermal annealing (100°C, 20min)		
Samples	G Band (cm ⁻¹)	FWHM (G) (cm ⁻¹)	Samples	G Band (cm ⁻¹)	FWHM (G) (cm ⁻¹)
G1	1601.74	10.46	G1	1601.03	11.76
G2	1592.84	10.63	G2	1591.67	10.09
Samples	2D Band (cm ⁻¹)	FWHM (2D) (cm ⁻¹)	Samples	2D Band (cm ⁻¹)	FWHM (2D) (cm ⁻¹)
G1	2702.69	30.97	G1	2691.51	31.40
G2	2700.89	34.09	G2	2690.96	31.18

5.6.4. Electrical characterization

It is known that theoretical studies predict a graphene mobility of 200,000 cm²V⁻¹s⁻¹ [Lin et al. 2013]. In this section, electrical properties of our CVD graphene have been studied in terms of sheet resistance, resistivity, carrier density and mobility. These electrical characterizations have been performed directly on monolayers of graphene transferred to SiO₂/Si substrates. Moreover, for these electrical characterization techniques, processing the samples by means of a photolithography step was required such in the case of the Transmission Line Method (TLM).

For this measurement, graphene pads need to be defined by using a mask and a photolithography step. For typical III-V semiconductors, the processing of TLM pads is not an issue. But for the particular case of working with graphene, special care has to be paid.

5.6.4.1. TLM measurements: sheet resistance and graphene/metal resistance

The contact resistance between graphene and the metal electrodes is key for the proper performance of graphene-based devices. In our particular case both the graphene/metal interface and the graphene/semiconductor interface are of special interest.

To start with, the study of graphene sheet resistance and graphene/metal contact resistance is presented in this section. With this purpose, TLM patterns (graphene/SiO₂/Si) already described in the previous section were manufactured. In relation to the metal used, Cr and Ti have been proposed to form an adhesion layer since they exhibit an excellent adhesion to SiO₂ substrates [Balci et al. 2012, Dai 2002]. Different metallization on graphene have been studied such as Cr/Au, Ti/Au, Ti/Pd/Au, Ti/Pt, Ni [Blake et al. 2009, Nagashio et al. 2010, Palacios et al. 2010, Robinson et al. 2011]. Ti/Pt gives similar contact resistance than Cr/Au contacts. Ti/Pd/Au give contact resistances in the range $0.5 \cdot 10^{-4}$ – $1 \cdot 10^{-4} \Omega \cdot \text{cm}^2$. However, there is still no consensus as to which one provides the lowest contact resistance. Besides, graphene/metal contact resistance is influenced by various facts: metal roughness rather than the metal work function, metal evaporation (e-gun, thermal evaporation, sputtering), graphene residues and so on [Watanabe et al. 2012].

An example of a simple TLM pattern with the metal pads contacts on top of the graphene monolayer is shown in Figure 5.19 a. W is the width of the pad, d the length of the pads and ℓ is the distance between the pads.

Figure 5.19 a) Sketch of a graphene TLM pattern with metal pads. The distances between pads (l) in this work are 90, 180, 360, 720 and 1440 μm . b) Plot of the total contact resistance (R_T) as a function of the pads separations (l). Contact resistance (R_c) and graphene sheet resistance (R_{SH}) can be directly obtained from the intersection and the slope of the linear fit respectively.

By injecting a current between two metal pads and measuring the resulting voltage, the total resistance of the different components can be obtained. By plotting the total resistance versus the distance between each pad we can obtain several parameters (*Figure 5.19 b*). R_c which is defined as the contact resistance and it is associated with the metal/semiconductor interface (in this particular case with the metal/graphene interface), and R_{SH} which is the sheet resistance of the graphene layer and R_m which is the resistance of the metal contact. In most situations, the metal resistivity of the contact is so low that $R_m \ll R_c$ that it can be neglected, so the total resistance is expressed:

$$R_T = 2R_c + \frac{R_{SH}}{W} l \quad \text{Eq 5.1}$$

Moreover, if we continue analyzing *Eq 5.1* the relation between R_T and l , provides the result of the so called specific contact resistance (ρ_c) by taking into account the transfer length L_T . The transfer length is defined as the average distance that an electron travels in the semiconductor beneath the contact (in this case graphene) before it flows up into the contact. This means that the current flow in the contacts is not uniform, being more important at the edges.

$$R_T = 2 \frac{R_{SH} L_T}{W} + \frac{R_{SH}}{W} l \quad \text{Eq 5.2}$$

$$L_T = \sqrt{\frac{\rho_c}{R_{SH}}} \rightarrow \rho_c = R_c W L_T \quad \text{Eq 5.3}$$

Reactive Ion etching technique (RIE) was performed at several centers such as Instituto de Sistemas Optoelectrónicos y Microtecnología or Instituto de Microelectrónica y Nanotecnología (Madrid). RIE has been used in order to isolate TLMs pads to get rid out of possible lateral deviation of the current through the TLM pad. The parameters used varied between the range of 5-70W from 30-120s in O_2 plasma. From the optical microscope, RIE parameters seem adequate since a proper graphene definition of pads can be observed (*Figure 5.14 c*).

The resistivity (ρ) of a graphene monolayer was directly calculated once the graphene sheet resistance (Ω/sq) was obtained from the TLM measurements. Taking into account the lateral direction of the electric current (*Figure 5.20*) and the nominal graphene monolayer thickness ($\sim 0.335\text{nm}$), ρ is given by:

$$\rho = R_{SH} \frac{A}{l} \rightarrow \rho_{\text{graphene}} = R_{SH} \cdot 0.335\text{nm} \quad \text{Eq 5.4}$$

Figure 5.20: Sketch of the current direction for the calculation of graphene resistivity.

Table 5.8: Summary of CVD graphene electrical parameters obtained by TLM devices.

One monolayer graphene samples	Substrate	Metallization Tool	Metals	Thickness (nm)	R_{SH} (Ω/sq)	Specific Contact resistance ($\Omega \cdot cm^2$)	Graphene resistivity ($\Omega \cdot cm$)
Company 1	SiO ₂ /Si	e-gun	Ti/Pd/Au	5.5/45/110	726.09	$2.8 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$
Company 1	SiO ₂ /Si	e-gun	Ti/Pd/Au	5/45/50	468.28	$7.8 \cdot 10^{-3}$	$1.6 \cdot 10^{-5}$
Company 1	SiO ₂ /Si	e-gun	Ti/Pd/Au	10/45/250	341.80	$5.5 \cdot 10^{-4}$	$1.1 \cdot 10^{-5}$
Company 2	SiO ₂ /Si	Joule	1.5nm Al Ti/Pd/Au	3/45/15	302.36	$4.5 \cdot 10^{-3}$	$1.0 \cdot 10^{-5}$
Company 2	SiO ₂ /Si	Joule	1.5nm Al Cr/Au	4/200	169.87	$4.2 \cdot 10^{-2}$	$5.7 \cdot 10^{-6}$

Summarizing in this section, graphene resistivity has been obtained by TLM measurements within the range of $2.4 \cdot 10^{-5}$ - $5.7 \cdot 10^{-6} \Omega \cdot cm$. The comparison with some metals resistivity from the literature such as silver, gold or platinum ($\rho_{Ag} \sim 1.47 \cdot 10^{-6} \Omega \cdot cm$, $\rho_{Au} \sim 2.44 \cdot 10^{-6} \Omega \cdot cm$, $\rho_{Pt} \sim 1.06 \cdot 10^{-5} \Omega \cdot cm$) confirms its great potential for its integration in optoelectronic devices since it has a resistivity close to these metals but with the advantage of its high optical transparency since it is just one atom thickness. On the other hand, contact resistance at graphene/metal interface has been found to be related to the metal deposition method as well as by the graphene quality. From Table 5.8, the best contact resistance obtained in our study was $2.8 \cdot 10^{-4} \Omega \cdot cm^2$ for an e-gun evaporation with 5.5nm Ti/45nmPd/110nmAu metallization with is close to what was found in literature [Chen et al. 2011]. With the aim of improving such result (up to typical values between $1.0 \cdot 10^{-5}$ – $5.0 \cdot 10^{-5} \Omega \cdot cm^2$ for our conventional AuGe/Ni/Au metallization used in our TJSC), as a future work, RTA processes or low power O₂ plasma treatment just prior to metal deposition followed by heat treatment will be investigated since it had been observed to improve the specific contact resistance considerably [Robinson et al. 2011].

5.6.4.2. Hall-Van-der-Pauw measurements: sheet resistance, mobility and carrier concentration

This section is focused on the study of the electrical characterization of graphene by using the Van der Pauw technique (VdP) and Hall measurements (carried out at MIT during the stage period). In this way and together with TLMs patterns, other electrical parameters such as graphene mobility and sheet density can be obtained.

It has been reported that the best graphene mobility is obtained for exfoliated graphene. On the contrary, for CVD graphene the mobility varies with domain sizes. The mobility of domain sizes of 6-20 μm (which is the order of our graphene grain size) have been measured between 800-7000 $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$ and even higher for bigger domain sizes [Fang et al. 2014]. Moreover, the mobility of graphene on SiO_2 at low and room temperatures is limited by impurity scattering, probably due to charged impurities in the SiO_2 substrate [Chen et al. 2008, Ishigami et al. 2007, Jang et al. 2008].

With the VdP technique, graphene sheet resistance (R_{SH}), mobility (μ) and sheet density (n_s) can be evaluated by using Eq 5.5 and Eq 5.6 where q is the elementary charge ($\sim 1.602 \cdot 10^{-19} \text{C}$), V_H the Hall voltage, I the current ($\sim 1\text{mA}$) and B the magnetic field applied perpendicularly to the plane of the sample ($\sim 2900 \text{ Gauss}$).

$$\mu = \frac{|V_H|}{R_{\text{SH}} \cdot I \cdot B} = \frac{1}{q \cdot n_s \cdot R_{\text{SH}}} \quad \text{Eq 5.5}$$

$$n_s = \frac{I \cdot B}{q \cdot |V_H|} \quad \text{Eq 5.6}$$

Figure 5.21: Sketch of a simple design of the Van der Pauw and Hall measurement used as an in situ characterization of CVD graphene after the wet transfer method at MIT.

VdP measurements were performed after the graphene wet transfer at MIT during the PhD stage by using a homemade VdP set-up. For simplicity, no photolithography step was applied. Instead, a silver paint was used as an ohmic contact pad for measuring sheet resistance by applying it on 4 edges of square shape transferred graphene (*Figure 5.21*).

Table 5.9: Summary of graphene electrical parameters obtained by VdP technique at 0° and rotating the sample 90°. Graphene samples were grown by CVD and transferred by wet transfer method at MIT during the exchange stage of the PhD.

<i>Samples</i>	<i>Thermal annealing</i>	<i>0° R_{SH} (Ω/sq)</i>	<i>0° Mobility (cm²V⁻¹s⁻¹)</i>	<i>0° N_s(cm⁻²) holes</i>	<i>90° R_{SH} (Ω/sq)</i>	<i>90° Mobility (cm²V⁻¹s⁻¹)</i>	<i>90° N_s(cm⁻²) holes</i>
<i>G1_1MLG</i>	NO	1181.6	794.	6.64 10 ¹²	1104.3	786.1	7.18 ·10 ¹²
<i>G1_1MLG</i>	380°C 1h	646.1	1559.4	6.19 10 ¹²	682.7	1315.9	6.94 ·10 ¹²
<i>G1_2MLG</i>	380°C 1h	568.5	2156.0	5.09 10 ¹²	553.6	2509.9	4.49 ·10 ¹²
<i>G2_1MLG</i>	380°C 1h	608.4	1083.9	9.46 10 ¹²	583.2	387.9	2.75 ·10 ¹³
<i>G2_1MLG_B</i>	380°C 1h	1476.5	2153.1	1.96 10 ¹²	1478.5	1841.8	2.05 ·10 ¹²
<i>G4_1MLG_C</i>	380°C 4h	423.4	1119.5	1.21 10 ¹³	416.7	1120.3	1.31 ·10 ¹³
<i>G4_1MLG_B</i>	380°C 4h	585.2	1671.8	6.4 10 ¹²	576.0	1660.6	6.52 ·10 ¹²
<i>G5_1MLG_A</i>	380°C 4h	453.3	989.5	1.4 10 ¹³	448.6	990.1	1.40 ·10 ¹²
<i>G5_1MLG_B</i>	380°C 4h	590.6	1681.6	6.3 10 ¹²	587.8	1501.8	7.11 ·10 ¹²

Table 5.9 summarizes the electrical parameters obtained for several graphene samples with different thermal annealings. In order to get an accurate result, samples were measured twice (at 0 degrees and rotating the sample 90°). As expected, graphene electrical properties were quite similar in both sample orientation. Only one big deviation is observed for sample G2_1MLG that could be related to some measurement artefact or error. Just for curiosity, it should be mentioned that due to the high humidity levels inside the lab, a moisture inhibitor was needed in some circumstances. What is concluded from these results is that a thermal annealing must be employed as a final step in order to improve graphene electrical properties. The final hole doping level for all samples, confirm the intrinsic p-type doping always present for CVD graphene transferred by the wet transfer method [Chen et al. 2007, Suk et al. 2013]. The graphene mobility is in agreement with the graphene grain size of 10-20µm [Fang et al. 2014]. At the same time, the variability observed in the mobility agrees with the dispersion values reported for CVD graphene. This may be explained due to the fact that the measurement does not take place within a single graphene domain, being more possible an interdomain measurement where the effects of the grain boundaries are present [Avouris et al. 2012].

Besides, additional VdP measurements were carried out in samples supplied from two companies. *Table 5.10* presents a comparison between graphene samples fabricated at MIT lab and the graphene samples from those companies. Again, similar p-type density levels between $1.0 \cdot 10^{12} - 3.2 \cdot 10^{13} \text{cm}^{-2}$ are found. As expected, graphene sheet resistance is reduced as long as the intrinsic p-type doping level achieved after the wet transfer method is increased.

Table 5.10: Comparison of some of the CVD graphene samples prepare at MIT together with another CVD graphene samples from two different companies.

<i>samples</i>	<i>Thermal annealing</i>	R_{SH} (Ω/sq)	<i>Mobility</i> ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	N_s (cm^{-2}) <i>holes</i>
<i>MIT_G1_1MLG</i>	NO	1143.0	790.3	$6.91 \cdot 10^{12}$
<i>MIT_G1_1MLG</i>	380°C 1h	664.4	1437.6	$6.57 \cdot 10^{12}$
<i>MIT_G1_1MLG</i>	380°C 1h	561.1	2332.9	$4.79 \cdot 10^{12}$
<i>MIT_G2_1MLG</i>	380°C 1h	1477.5	1997.5	$2.00 \cdot 10^{12}$
<i>MIT_G4_1MLG_C</i>	380°C 4h	420.1	1119.9	$1.25 \cdot 10^{12}$
<i>MIT_G4_1MLG_B</i>	380°C 4h	580.1	1666.2	$6.45 \cdot 10^2$
<i>MIT_G6_1MLG</i>	380°C 4h	347.3	1076.5	$1.66 \cdot 10^{13}$
<i>Graphenea_1MLG</i>	YES	273.7	1083.7	$2.11 \cdot 10^{13}$
<i>Graphenea_1MLG</i>	YES	281.7	1052.0	$2.10 \cdot 10^{13}$
<i>Graphenea_2MLG</i>	YES	164.7	754.7	$5.02 \cdot 10^{12}$
<i>Graphenea_2MLG</i>	YES	159.9	1200.8	$3.25 \cdot 10^{13}$
<i>Company 2</i>	?	1131.0	532.3	$1.01 \cdot 10^{13}$

Finally, *Figure 5.22* summarizes the mobility values as a function of doping density for CVD graphene samples presented along this document together with other CVD graphene samples synthesized at different laboratories and conditions. Nevertheless, from these different works it can be observed that there is a high carrier density mobility degradation from the expected intrinsic properties of graphene which is attributed to short range scatters [Castro Neto et al. 2009, Chen et al. 2007, Geim et al. 2007]. Moderate CVD graphene mobility obtained in this work could be related to the presence of the already mentioned domain boundaries, and the presence of wrinkles and other residual defects originated mainly during the wet transfer process. At the same time, graphene devices on standard SiO_2 substrates exhibit electrical properties lower than in suspended graphene due to different facts such as the detrimental influence of dangling bonds, charge traps, roughness, chemical reactivity. It is normally assumed that the dominant source of scattering in graphene is due to charged impurities in the substrate. As an example, the improvement of the electronic quality of graphene has been obtained with the use of alternative

substrates such as boron nitride [Dean et al. 2010]. On the contrary, other studies remark that this is not the limiting mechanism [Ponomarenko et al. 2009].

Figure 5.22: Comparison of the electrical Mobility (μ) of CVD graphene versus carrier concentration (n_s) from various growth mechanisms such as copper substrate at low pressure (blue cross), nickel substrate at atmosphere pressure (red triangle), synthesized graphene on SiC-Si face (orange cross), the effect of dopants such as Aluminum oxide (green circle) and the CVD graphene of this Thesis (pink circle). Black lines (continuous, dash and dots) represent the theoretical performance of mobility for different graphene quality (μ_0, C). Reprinted from [Hsu et al. 2012]

5.6.4.3. Graphene doping

5.6.4.3.1. Introduction

Selective doping of graphene and thus tuning graphene Dirac point has been paid a tremendous attention since it determines the final performance of integrated graphene in most electronic applications.

Theoretical studies have shown that at the Dirac point the density of states is zero, resulting in a low conduction for undoped graphene. However, the Fermi level of graphene can be tuned by doping. There are several ways of doping graphene, namely: a) by applying an electric field [Yu

et al. 2009], b) by metal contacts [Pi et al. 2009], c) by applying some chemicals like NH_3 [Das et al. 2008, Pirkle et al. 2011], AuCl_3 [Kwon et al. 2012], aromatic molecules, water or ammonia on the surface [Wang et al. 2009], potassium nitrate (KNO_3) [Khan et al. 2014] and so on.

Doping graphene in a p-type behavior is much easier than n-type due to the fact that native graphene behave as a p-type semi-metal [Levesque et al. 2011]. Since for the application of graphene on our solar cells, an n-type graphene would be desirable, we have explored paths to achieve n-type graphene. We have chosen in this thesis chemical modifications of graphene as the first approach. Specifically, the use of organic molecules that can be absorbed on graphene provides a promising approach to control the carrier type and concentration. For this purpose, we have used organic molecules such as poly(vinyl alcohol) (PVA) and polyethylenimine(PEI). In parallel, a simple approach consisting on the thermal evaporation of a few nanometers of aluminum was also investigated.

5.6.4.3.2. Graphene carrier density modification by Aluminum deposition

It is known that at the interface between two materials, the difference in work function will be a key factor in determining how electrons will be transferred. Since aluminum work function ($\Phi \sim 4.28\text{eV}$) is lower than graphene work function ($\Phi \sim 4.6\text{eV}$), it is expected that graphene will act as an acceptor of electrons. So, the first method used to try to dope graphene n-type was by evaporating a thin layer of aluminum with a thickness of 0.5-2nm. Looking at *Figure 5.23*, it can be observed how graphene Fermi level would shift resulting in an n-type behavior.

Figure 5.23: Schematics of graphene Fermi level upshift as the result of the graphene/Al contact interface. Reprinted from [Shi et al. 2014].

Table 5.11: Summary of electrical parameters (R_{SH} , μ and N_s) of CVD graphene samples before and after the thermal evaporation of 0.5 and 2 nm of aluminum (Al) on top of it.

Samples	Aluminum thermal evaporation	R_{SH}	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	$N_s(\text{cm}^{-2})$ holes
G4_C	—	416.7	1120.29	$1.33 \cdot 10^{13}$
G4_C	0.5nm	475.6	679.39	$1.93 \cdot 10^{13}$
G4_A	—	439.7	898.81	$1.71 \cdot 10^{13}$
G4_A	2nm	470.1	931.87	$1.42 \cdot 10^{13}$

As it can be observed in Table 5.11, from VdP and Hall measurements, evaporation of a few nanometers of Al does not seem to induce an important change on the intrinsic hole doping of graphene layers which persist in a p-type doping concentration. Although recent works suggest the deposition of ~ 30 nm of Al_2O_3 on top of the aluminum may produce a better result since this layer would avoid further oxidation acting as a passivation layer to minimize the exposure to ambient [Shi et al. 2014].

This electrical characterization was complemented with Raman spectroscopy. It is reported that the shift of G and 2D position peaks towards lower wavenumbers is attributed to n-type doping while the shift towards higher wavenumbers is related to p-type doping in graphene layers [Singh et al. 2013, Singh et al. 2012]. However, the Raman spectrum of Figure 5.24 shows no shifts of the main two peaks, just a slight increase of the 2D peak after the evaporation of the thin Al layer which indicates that this is not the best option to modify the carrier concentration of CVD graphene.

Figure 5.24: Raman spectra of a graphene sample after its wet transfer to a SiO_2/Si substrate (black line) and after the deposition of ~ 2 nm of Al (red lines).

5.6.4.3.3. Graphene carrier density modification with polyethylenimine (PEI)

Polyethylenimine (PEI) with chemical formulation (C_2H_5N) contains amine groups which are suitable for n-type doping graphene [Cha et al. 2014]. Accordingly, we rinsed a graphene sample in a PEI (with low molecular weight from Sigma Aldrich) solution for 30-40 minutes. Afterwards it was rinsed in isopropanol (IPA) and dried with N_2 and heated at $80^\circ C$ for 5 minutes to remove the solvent. Additionally, one sample was kept in acetone for 1h30 for comparison purposes.

Table 5.12 : Summary of electrical parameters (R_{SH} , μ and N_s) of CVD graphene samples before and after PEI coating.

Samples	PEI	R_{SH} (Ω/sq)	Mobility ($cm^2V^{-1}s^{-1}$)	N_s (cm^{-2}) holes
G6	—	347.07	1076.00	$1.66 \cdot 10^{13}$
G6	30' PEI	386.33	1015.50	$1.59 \cdot 10^{13}$
G6	40' PEI + 1h30' acetone	975.67	2040.46	$3.13 \cdot 10^{12}$

Table 5.12 presents the electrical parameters of the graphene layer after PEI coating. As it can be observed, only the sample that was rinsed in acetone as a final step exhibited a bigger change in the final doping and thus in the electrical properties of graphene. To further analyze the effect of the PEI coating on graphene, Raman spectroscopy was used again for samples with and without PEI coating. Analyzing Figure 5.25 the downshift of both G and 2D peaks confirms the decrease of the hole doping which still remains quite high. Moreover 2D peak is also increased which is another evidence of doping decrease.

Figure 5.25: Left) Raman spectra of a graphene sample after its wet transfer to a SiO_2/Si substrate (black line) and after the PEI coating for 30 minutes (red line). Right) Magnification of the 2D peak which suggests a carrier concentration change.

The fact that a significant decrease of the hole doping is not achieved can be based on the instability of n-type dopants [Schedin et al. 2007]. Future works will be carried out concerning some works found in the literature where the isolation of this PEI layer by another graphene layer had been found to be used to isolate and preserve PEI properties to act as an n-type for a longer period of time [Cha et al. 2014].

5.6.4.3.4. Graphene carrier density modification with poly(vinyl alcohol) (PVA)

As the third method, poly(vinyl alcohol) (PVA) which is an hydroxyl anion rich polymer, was used in order to change carrier density in our CVD graphene samples. The PVA solution was prepared by dissolving 2%-4%wt of PVA powder in deionized water. Afterwards, this polymer film was deposited on top of the graphene/SiO₂/Si samples by spin-coating at 2000 rpm for 60s and baked at 90°C for 5 min.

Again the doping effect of graphene samples coated with PVA was examined with VdP and Hall measurements. As it can be observed in Table 5.16, graphene sheet resistance increases when PVA is deposited as a consequence of the reduction of carrier concentration. Taking into account these results, PVA could be considered as a candidate to try to reduce the intrinsic hole doping of CVD graphene although it is still far away of achieving an n-type behavior.

Table 5.13: Summary of electrical parameters (R_{SH} , μ and N_s) of CVD graphene samples before and after PVA coatings.

Samples	PVA Solution concentration and time	R_{SH} (Ω/sq)	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	N_s (cm^{-2}) holes
G5_A	—	450.94	989.81	$1.39 \cdot 10^{13}$
G5_A	2% 2h	735.36	1368.51	$6.20 \cdot 10^{12}$
G5_B	—	589.21	1591.73	$6.68 \cdot 10^{12}$
G5_B	2% 18h	1353.8	3268.28	$1.41 \cdot 10^{12}$

Additionally interesting works have been found in relation to the use of PVA coatings. By increasing the PVA concentration together with heat treatments, an n-type behavior could be achieved [Kim et al. 2015].

Figure 5.26: Comparison of 2D and G bands positions versus PVA concentration. Blue circles and triangles corresponds to the Raman peaks obtained along this work, while black squares and triangles correspond to the Raman peaks obtained in [Kim et al. 2015]. Even if the behavior of the PVA coating effect is the same, the wavenumber of the peaks is not the same for each work. This could be related to the influence of several facts such as laser excitation, together with the carrier density in each sample and the influence of the substrate.

5.6.4.3.5. Conclusions from n-type doping

It can be concluded that n-type doping graphene is quite challenging. The three methods that have been studied in this section have resulted in a decrease of the p-type density although no n-type doping has been reached. At the same time, the graphene sheet resistance increases due to the reduction of carrier concentration. Even if n-type doping graphene could be achieved as reported in literature [Cha et al. 2014, Kim et al. 2015, Singh et al. 2013], one possible drawback of chemical doping would be the return from an n-type behavior to a p-type behavior since they rapidly oxidized due to the presence and the adsorption of water molecules or oxygen in air.

Raman spectra performed on graphene samples after the intentional doping with Al, PEI and PVA methods show that graphene carrier density was actually modified with the corresponding hole doping reduction for all cases. Table 5.14 summarizes the position together with the FWHM of G and 2D peaks with and without intentionally doping for the three doping mechanisms. For a better visualization the down-shift of the G peak together with the increase of the FWHM due to the density carrier reduction, is represented in Figure 5.27. Moreover, preservation of graphene quality layers was confirmed since no D peak signal appears after chemical doping as a consequence of damage or introduction of defects on the graphene samples. This is not the case of other intentional doping mechanisms where graphene structure can be modified [Georgakilas et al. 2012, Rao et al. 2010].

Table 5.14: Summary and comparison among the main graphene Raman peaks (G and 2D) with the intrinsic doping level achieved (after the CVD and wet transfer steps) and after intentional doping with Al, PEI and PVA coatings.

Samples	Intrinsic Doping		Intentional Doping		
	G Band (cm^{-1})	FWHM (G) (cm^{-1})	Dopant	G Band (cm^{-1})	FWHM (G) (cm^{-1})
Gc	1595.65	9.52	PVA	1588.46	11.99
G4	1601.81	11.32	Al	1597.03	14.36
G6	1605.86	10.31	PEI	1596.68	15.96

Samples	Intrinsic Doping		Intentional Doping		
	2D Band (cm^{-1})	FWHM (2D) (cm^{-1})	Dopant	2D Band (cm^{-1})	FWHM (2D) (cm^{-1})
Gc	2688.39	31.2	PVA	2683.21	34.64
G4	2690.92	33.9	Al	2687.06	38.69
G6	2697.10	34.85	PEI	2689.88	41.00

Figure 5.27: Plot of the FWHM of the G peak as function of its position (obtained by Raman spectroscopy) influenced by the density carrier in the graphene layer modified by the intentional doping with Al, PVA and PEI coatings. This plot agrees with Raman studies that demonstrated the sensitivity of phonon vibrations in graphene due to its doping level [Wang et al. 2009].

5.6.5. Optical characterization

5.6.5.1. Introduction

Graphene optical properties suggest the suitability of graphene as a good candidate to be used as a transparent electrode for solar cells and light-emitting diodes (LEDs) [Gao et al. 2011, Kumar et al. 2010, Wan et al. 2011]. As it has been already explained, graphene properties are influenced by the synthesis method, the transfer technique and by the target substrate where it is transferred. In this situation, a complete optical characterization of our CVD graphene is required.

Accordingly, in this section we present the determination of the refractive indexes (n , k) from ellipsometry measurements together with measurements and simulations of reflectance, transmittance and absorptance of 1-3 CVD graphene monolayers. With these results we will be able to assess the impact of graphene absorption and reflection of our TJSC.

5.6.5.2. Determination of refractive index and extinction coefficient of CVD graphene by ellipsometry

The aim of this subsection is to determine the refractive index (n) and the extinction coefficient (k) of our CVD graphene. For this purpose, we have taken into account the already mentioned effects of: a) interactions between graphene and substrate, b) stacking more than one monolayer of graphene, c) the residues from the transfer process that could degrade the properties of graphene and the accuracy of the measurements and d) the thermal treatment.

With this purpose, Spectroscopy Ellipsometry (SE) was carried out at the University of Málaga. Measurements were performed with a variable angle of 60° - 75° for a photon energy range between 1.5-5 eV. Moreover the spot size of the ellipsometer varies between 1 and 4 mm depending on the incident angle and signal to noise ratio, so the probability of measuring a distribution of monolayer and bilayer regions was also taken into account.

Concerning SE analysis and fitting procedures, the thicknesses of the different layers of the structure to be analyzed can be treated as known parameters or they can be part of the final result of the ellipsometry fitting process. In our particular case, the structures were previously characterized by ARXPS (section 5.5.4) and are called MLG, MLG on TO and BLG as summarized in Table 5.15. According to this, the real layered structure determined by ARXPS has been as input in the ellipsometry analysis.

Table 5.15: Summary of the layered structure of the CVD graphene samples transferred by the wet transferred method used for this study.

<i>Samples name</i>	<i>Graphene</i>	<i>SiO₂ /Si</i>
MLG	1MLG	Native oxide
MLG on TO	1MLG	Thermal oxide ~300nm
BLG	2MLG	Native oxide

Regarding the native silicon oxide on top of the silicon substrate for both MLG and BLG samples, SE measurements were performed in the region without graphene coverage, resulting in an oxide thickness of ~2.6 nm and ~3.4 nm, respectively.

The fitting analysis were done at the University of Málaga by a Semilab Ellipsometric Analysis (SEA) version 1.3 from SEMILAB. The graphene layers have been modeled with a Lorentz oscillator for the van Hove singularity [Nelson et al. 2010]. The behavior in the near-infrared (NIR) region is represented by the Drude model [Lee et al. 2011] which can be used to describe the electrical conduction of quasi free electrons in metals or carriers in semiconductor materials. This model leaves five general terms which should be adjusted. Information about the adjustments and the final parameters of the SE model used to describe the optical properties for these different graphene samples are detailed in [Ochoa-Martinez et al. 2015]. In a first approach (not presented in this document) fittings were done in the nominal structures (*Table 5.15*), without considering the contamination layers detected by ARXPS. Furthermore, a graphene thickness variation from 0.335-0.53nm was considered. Only when the real stack revealed by ARXPS was taken into account, a proper fitting was achieved in the whole wavelength range. Additionally, the possibility of having non-uniform graphene monolayer was also considered. The data fitting for the MLG results in an effective medium approximation (EMA) interlayer of around 1.1 nm, and a water top layer of ~ 0.6 nm (see *Figure 5.28* left). This EMA interlayer suggest the presence of water molecules, PMMA residues but also the presence of a 5% of the area with more than one monolayer graphene [Ochoa-Martinez et al. 2015].

Figure 5.28: Sketch of the layer structure of MLG (left) and BLG (right) transferred on a native SiO₂/Si substrate. Determination of the real thickness of the layers were obtained by complementary ARXPS and SE measurements.

Following the same procedure, SE measurements and data fittings were carried out (helped by the already optimized MLG model) on the bilayer (BLG) and monolayer graphene on thermal oxide SiO₂/Si substrate (MLG on TO) samples. In this case, a thicker silicon oxide layer ~ 3.4 nm and a thicker water layer ~ 0.6 nm on top of graphene (see *Figure 5.28* right) was obtained which is also in agreement with ARXPS results (section 5.5.2).

Finally, *Figure 5.29* shows the good ellipsometry data fittings (left) together with the n and k achieved (right).

Figure 5.29: Left) Ellipsometry measurements and fitting at 75° angle for CVD graphene deposited in different Si₂O/Si samples. Green line represents the measurement of a Si₂O/Si substrate without graphene. Right) Resultant refractive index (n) and extinction coefficient (k) of our graphene.

As a final point, thermal treatments (150°C-250°C for one hour) were performed on the MLG sample prior to the subsequent characterization by SE. This time, data fitting revealed a reduction of EMA layer by half [Ochoa-Martinez et al. 2015]. At the same time, it is known that since graphene monolayer is almost one atom thick, the ability of trapping water molecules form the ambient is very high. This was further confirmed by measuring again by SE after some days, revealing that the EMA layer thickness had already increased.

5.6.5.3. Determination of CVD graphene absorption by Reflectance and Transmittance measurements

In this section, the optical response of large scale CVD graphene, have been analyzed through Transmission ($T(\lambda)$) and Reflection ($R(\lambda)$) spectra measurements from the visible up to the middle infrared range with a Perkin Elmer lambda 1050 Spectrometer.

With the intention of studying the impact of transferring a CVD graphene monolayer on a substrate of interest such as a semiconductor layer (in particular, the AlInP window layer, which is the top layer of a triple junction solar cell), a set of structures were grown by MOVPE (see Figure 5.30 a).

First of all, the GaAs top layer was chemically etched by NH₄OH:H₂:H₂O₂:H₂O (2:1:10). Then the top AlInP layer (layer of interest (LOI)) was glued to a glass holder with a transparent epoxy resist. After that, the subsequent etching of the rest of the layers (starting from the GaAs substrate) was done with NH₄OH:H₂:H₂O₂:H₂O (2:1:10) for arsenide layers and with HCl for phosphide

layers. The total etching of the layers takes $> 1\text{h}$ due to long duration of the substrate etching step (etching of $\sim 375\mu\text{m}$ GaAs).

Figure 5.30: a) Sketch of the AlInP structures grown for this experiment. Due to MOVPE aspects (no relevant for this study), each structure needs to be capped with an epitaxial GaAs layer. In order to get physical access to the layer of interest (AlInP), a stop-etching layer (SEL) of GaAs was grown. b)) Sketch of the bare substrate (AlInP layer) before graphene deposition on top of it.

For the sake of simplicity, the final stack formed by an AlInP layer, a transparent epoxy and a glass holder will be called along this section “bare substrate” which is sketched in Figure 5.30 b). Thus, the AlInP layer will be the first layer seen by the light impinging the bare substrate.

It must be mentioned that the first batch of measurements (Batch 1) performed on the samples consisted on the R and T measurements done directly on the bare AlInP substrates from 350-2500nm prior to graphene deposition. Subsequently, two of the bare substrates were kept without graphene deposition (2037_B, 2042_B) while the other three (2037_A, 2042_A and 2042_C) were covered with graphene monolayers (see Table 5.16).

Table 5.16: Summary of the III-V semiconductor samples used for R , T analysis covered with and without CVD graphene monolayer transferred by the wet method.

Structures	material	Thickness (nm)	Graphene monolayer
2037_A	AlInP	~ 215	2MLG
2037_B	AlInP	~ 215	–
2042_A	AlInP	~ 215	1MLG
2042_B	AlInP	~ 215	–
2042_C	AlInP	~ 215	3MLG

Figure 5.31: a) Experimental Reflectance (R) and b) Transmittance (T) measurements of $\sim 230\text{nm}$ AlInP samples without graphene (pink dots) and with 1MLG (blue dots), 2 MLG (green dots) and 3 MLG (black dots), respectively. c) Reflectance plot zoom for the 300-400 nm range.

Following with the experiment, once graphene has been transferred to some bare substrates, R and T was measured again for all them (Batch 2). Since the R and T results for the bare substrates without graphene were the same in both batches (Batch 1=Batch 2), it was concluded that R and T measurements performed on the samples containing graphene (prior and after graphene deposition) were accurate enough to be compared. Reflectance and transmittance for the structures of Table 5.13 is presented in Figure 5.31. For reflectance measurements, the most significant change is appreciated for lower wavelengths (300-400nm) where the reflectance signal is reduced as long as the number of graphene layers is further increased (Figure 5.31 c).

Looking in more detail the visible range (Figure 5.32), the incorporation of one graphene monolayer does not seem to affect significantly the reflectance. On the contrary, a slight reflectance decrease together with a small energy shift can be appreciated when two graphene monolayers are incorporated. The experimental data fitting at the visible range also confirm this behavior (see Figure 5.32).

Figure 5.32: Experimental (top) and experimental data fitting (bottom) of some of the structures of Table 5.13 to detect the impact of the transfer of 1 and 2 graphene monolayers. The data fitting perfectly agrees with the experimental. However, an intensity variation between experimental and simulations is observed. We think this is because of a possible overestimation of the experimental reflectance due to a shift error in the reflectance set-up.

On the other hand, the fitting is achieved for a thickness variation of 2nm between the AlInP layers. In order to discard a possible influence of this thickness variation together with a difference on the epoxy thickness among the structures, a second simulation for a specific AlInP/epoxy/glass substrate with one and two graphene monolayers was performed (Figure 5.33). As it can be observed, 2 graphene monolayers (together with the EMA interlayers) slightly influence on the reflectance with a very low reflectance decrease and a very slight energy shift. At the same time, going back to the experimental reflectance measurements of Figure 5.32a since this reflectance change is in between the deviation between several measurements, we may assume that the impact of graphene on the reflectance of the AlInP sample is negligible. On the contrary, the structure (G/AlInP/epoxy/glass) transmittance is slightly reduced as long as the number of graphene monolayers is increased. Moreover, it must be mentioned that all these results may be affected by the roughness of the AlInP-epoxy-glass substrate.

Figure 5.33: Simulation of an arbitrary AlInP/epoxy/glass substrate (AlInP thickness of 214.5nm) reflectance as function of the graphene monolayers incorporation. For these simulations, the presence of EMA layers on top and between the graphene layers were also considered.

To further confirm the accuracy of the n and k optical parameters of our CVD graphene already obtained by ellipsometry spectroscopy, we used such values to simulate the experimental transmittance of AlInP samples with one monolayer on top of AlInP (1MLG-AlInP), with two monolayers graphene on top of AlInP (2MLG-AlInP) and with three monolayers graphene on top of AlInP (3MLG-AlInP). Additionally, optical parameters (n , k) of the AlInP layer, the glass holder and the epoxy used along the experiment were also determined from by ellipsometry.

By using the Generalized Transfer Matrix Method [Centurioni 2005], the transmittance fits were performed. As Figure 5.34 shows, the data fittings are very good except for the 500-525 wavelength range even without graphene. The difference between experimental and simulated transmittance observed at such wavelength where the AlInP bandgap is, can be related to the inaccuracy of the extinction coefficient data we manage near the AlInP band gap. Apart from that peak, experimental and simulations of the transmittance for the AlInP structures with and without graphene perfectly fit, thus confirming the accuracy of the optical parameters of graphene obtained from ellipsometry.

Figure 5.34: Experimental (black circles) and simulation (red lines) of the Transmittance (T) of $\sim 214\text{nm}$ AlInP samples with no monolayer graphene (a), with 1MLG-AlInP (b), with 2MLG-AlInP (c) and with 3MLG-AlInP (d) respectively

From the experimental measurements (dots in Figure 5.34), the relative transmission of graphene ($T_{N_{MLG}}(\lambda)$) was obtained by using the transmittance of the bare substrate for its normalization Eq.5.11. Once we have measured the transmittance of the bare AlInP substrate without graphene $T_{substrate}(\lambda)$ and also the transmittance of the different AlInP bare substrates covered with 1 to 3 graphene monolayers on top ($T_{N_{MLG}+substrate}(\lambda)$), the relative transmittance of the individual graphene monolayers ($T_{N_{MLG}}(\lambda)$ ($N=1,2,3$ graphene monolayers)) can be calculated by using the substrate transmittance as:

$$T_{N_{MLG}}(\lambda) = \frac{T_{N_{MLG}+substrate}(\lambda)}{T_{substrate}(\lambda)} \quad \text{Eq. 5.1}$$

The results are shown in Figure 5.35 where again oscillations due to Fabry-Perot interference with the substrate are observed.

Figure 5.35: Relative transmittance if 1-2-3MLG (blue, green, black dots respectively) deposited on an AlInP bare substrate.

In consistence with this experiments, a lot of interest on the study of graphene optical transmittance have been paid [Nair et al. 2008, Zhu et al. 2014]. In particular, it has been established that suspended graphene leads to the opacity¹³ $1-T=N\pi\alpha$, which is directly proportional to the number of layers (N). Where α is the fine structure constant ($1/137$), c the speed of light, e the electron charge, and $\hbar$ Planck constant. Thus, for one suspended monolayer graphene Eq 5.7 gives an absorption of 2.3% for a single layer graphene in the visible range [Kuzmenko et al. 2008].

$$\alpha = \frac{e^2}{\hbar c} \rightarrow 1 - T = \pi\alpha = 2.3 \cdot 10^{-2} \quad \text{Eq 5.7}$$

Since we are not completely sure about the experimental reflectance measurements (overestimated reflectance), absorptance of graphene was obtained from the transmittance fittings performed on the experimental data described in Figure 5.34. Accordingly, Figure 5.36 shows the absorption of several layers ($N=1,2,3$) of graphene on top of an AlInP substrate. The

¹³ Graphene's opacity is related to graphene absorbance and it is defined as $1-T$ where graphene reflectance is neglected ($< 0.1\%$). Graphene opacity yields $2.3 \pm 0.1\%$ being practically independent of wavelength (λ) in the visible range.

experimental average values of the graphene absorptance for one, two and three monolayers are 1.2% and 3.4% and 4.8%, respectively for 360-950nm range and 1.2%, 3.7%, 5.2% for the visible range (400-700nm).

Figure 5.36: Absorption of one, two and three monolayers of graphene on top of an AlInP semiconductor layer. The calculation of this absorption is obtained by simulations with OPTICAL software of the already transmittance fittings to the experimental transmission measurements.

Additionally, a higher absorption peak is obtained at the UV-region $\sim 4.65\text{eV}$ as theoretically predicted [Yang et al. 2009] which is related to the Van Hove singularity of graphene, which directly depends on graphene number of layers [Lee et al. 2011]. It can be observed how this asymmetric peak height is almost doubled for two monolayers graphene (see Figure 5.36). This interband absorption peak related to the resonant exciton enhances optical absorption at that energy range. Additionally, the peak is at 5.1 eV without electron-hole interaction, but it shifts down by 0.5 eV when electron-hole interaction is taken into account [Yang et al. 2009]. This increase of the optical absorption of graphene for the wavelength range of 200-350nm is not relevant since the irradiation levels of the ASTM G173-03 terrestrial solar spectrum relevant for MJSC (presented in Chapter 6) are almost negligible at that range.

As a result of the graphene absorption on top of AlInP, it can be concluded that these values are close to the theoretical average value of suspended graphene monolayer of around $\sim 2.3\%$ for the visible range being also a bit lower for our particular case (see Figure 5.36). This fact can be also

appreciated for both two and three monolayers. This result is also in consistence with [Lee et al. 2011] where band theory predicts a lower absorbance $1-T = 1.0 \cdot 10^{-2}$ and $1-T = 1.7 \cdot 10^{-2}$ for graphene on a silicon and shapire substrate since refractive index (n) is 3.4 and 1.76, respectively. In our work, an absorbance of $1.2 \cdot 10^{-2}$ has been achieved for one graphene monolayer on an AlInP substrate which has a refractive index close to silicon. All these results, suggest one more time the compatibility of integrating graphene in our MJSC structures.

5.7. Summary and conclusions

This Chapter describes the first contact with 2D materials such as graphene at IES-UPM. At the beginning of the chapter a brief description of the state of the art of graphene in solar cell applications is presented. Due to graphene exceptional properties, different solar cell architectures use graphene's potential to enhance its efficiency even more. A thorough electro-optical characterization of CVD graphene has been studied and evaluated in order to integrate graphene in our TJSC.

Firstly, graphene transfer by the wet transfer method together with graphene manipulation have been carefully analyzed, founding that all the steps done during this transfer method are crucial since they play an important role on the final electrical and optical graphene properties and thus, on its final quality.

Besides, the opportunity of growing high quality CVD graphene together with intentional doping mechanisms have been also performed at MIT during the Phd exchange period of three months. The close interaction of graphene and 2D materials in general with environment, such as the target substrate were it is deposited, absorption of chemicals, water, etc. have been carefully studied.

In addition to the development of the technology related to the growth and transfer of graphene, in this chapter the electrical and optical characterization of graphene layers is presented. TLMs, Van der Pau and Hall measurements confirm that CVD graphene used during this document is as good as other CVD graphene found in literature with mobility $\sim 750-2000(\text{cm}^2\text{V}^{-1}\text{s}^{-1})$, p-type density level between $1.0 \cdot 10^{12}$ - $3.2 \cdot 10^{13}\text{cm}^{-2}$ and sheet resistance of $\sim 300-500\Omega/\text{sq}$. Additionally, graphene optical transmittance was experimentally measured and simulated with an accurate fit which confirms that the n and k optical parameters obtained by ellipsometry spectroscopy are quite accurate. These optical parameters were obtained taking into account the real

graphene/substrate stack with including debris from the wet transfer method deduced by ARXPS measurements. These optical parameters were also useful in order to calculate the absorption of several graphene monolayers on top of the AlInP window layer used at the top of our MJSC structure. The absorption of one graphene monolayer on top of this semiconductor layer results in 1.2% and 3.7% for one and two graphene monolayers respectively for the visible range. These values are below the theoretical 2.3% (4.6%) of a suspended graphene monolayer (bilayer).

After this extended characterization, it can be concluded that graphene unique optical and electrical properties gives rise to its integration in a complete MJSC which is going to be addressed in Chapter 6.

Chapter 6

INTEGRATION OF GRAPHENE ON III-V CONCENTRATOR SOLAR CELLS

6.1. Introduction

At the beginning of this PhD document, concentrator multijunction solar cells (MJSC) were presented as the highest efficiency solar cells to date. Different MJSC architectures have been designed [Dimroth et al. 2014, France et al. 2015, Sabnis et al. 2012], but all of them exhibit a problem related to lateral series resistance that degrade the solar cell efficiency when working at high concentration levels. At the same time, as already mentioned in Chapter 5, due to the good electrical and optical properties of graphene, its integration in many kinds of solar cells has been investigated during the last years (organic, thin films, nanowires...). The aim of this chapter is to assess graphene integration on concentrator MJSC architectures and, particularly, on lattice matched GaInP/Ga(In)As/Ge triple junction solar cells - which is the structure studied along this thesis - in order to reduce the lateral series resistance at high concentration levels. Accordingly, this chapter describes both the graphene integration on concentrator solar cells and the characterization of these solar cells when 1-2 monolayers of CVD graphene are incorporated.

6.2. Graphene integration on III-V concentrator solar cells.

6.2.1. Introduction

Concentration solar cells make use of special front grid designs to handle very high density currents. The front grid used in this thesis for the integration of graphene in our solar cells is the inverted square configuration already used in previous chapters for the development of the triple junction solar cell with an active area of 1mm^2 . This configuration has been described in previous works in our group [Algora et al. 2000, Espinet 2012]. It consists on an inverted square geometry with a bus bar width of $100\mu\text{m}$, 8 to 11 evenly spaced fingers that are $3\mu\text{m}$ wide providing a shadowing factor (FS) between 2.7-3 % (see Figure 6.1).

Figure 6.1: Image of the inverted square front grid metallization used along this thesis and moreover for the integration of graphene on concentrator solar cells.

Two different approaches could be faced when integrating graphene in concentrator solar cells. The first approach is to do the deposition of graphene on top of the solar cell after its typical manufacturing. In this first approach, graphene is going to be in contact with both the top semiconductor layer (in this particular case the AlInP window layer) and the front contact grid. Therefore, this first approach adds the graphene integration step after the typical solar cell manufacture (excluding the mesa etching step). The second approach consists on the deposition of graphene on top of the active surface of the solar cell prior to the front grid metallization. Therefore, this second approach modifies the typical manufacturing process and also requires a different metallization suitable to reach ohmic contacts on graphene. Both approaches are interesting and present advantages and disadvantages. On the one hand, with the first approach, the front grid metallization that will be deposited and all the photolithography steps prior to mesa etching definition are not changed. This makes this approach easier to implement since all these

steps are already well known and developed in our group. On the other hand, with this first approach, graphene is not deposited on a planar surface since the bus bar and fingers (thickness of at least 800nm and typically of a few microns) are present in the active area making it more difficult to attain a good adherence of graphene on the whole surface. Regarding the second approach, graphene will be deposited directly on a planar surface, which provides a full coverage of the surface. At the same time, all the photolithography steps needed for the solar cell front processing will be done with the presence of this graphene monolayer, making it more difficult as has been already described in Chapter 5. Moreover, the usual metallization used for the front grid is not the optimum in this case since it will be directly contacted to graphene and different metals might need to be optimized.

Accordingly, we have developed the integration of graphene in a concentrator solar cell following the first approach, which means the deposition of 1-2 monolayers of graphene on top of the solar cell structure with the aim of enhancing the photocurrent extraction and thus solar cell performance at high concentrations.

6.2.2. Photocurrent extraction mechanisms with the use of graphene

As we have stated, we have integrated graphene in our cells on top of the whole structure as described in *Figure 6.2*. This means that graphene is transferred not only on top of the III-V semiconductor surface, but also on top of the front metallization, that for the case of this thesis is the AuGe/Ni/Au stack since it is the typical metallization used for our n-p TJSC structure. *Figure 6.2*, shows how photocurrent flows through different resistances when is extracted to the external connections.

As it has been already pointed out through this thesis, III-V multijunction solar cells operating under concentrated light exhibit losses mainly because of the presence of lateral series resistances. The main lateral series resistances are those of the front metal grid and top emitter/window. Therefore, on the one hand, the idea of depositing graphene on top of the cell is mainly to study the role that graphene could play and if it is able to extract vertically the photocurrent from the AlInP window layer, avoiding the lateral current flow to reach the front metal grid. On the other hand, graphene could also help in the photocurrent extraction by allowing an additional path in parallel to the front metal grid. Thus, the study of the resistances participating during the current extraction is essential.

Figure 6.2: Schematics of graphene integration on our TJSC. a) Graphene on top of both metallization and semiconductor active area. b) Zoom of a small portion of the solar cell with the main resistances participating in the photocurrent extraction (black). The additional resistances (red circles) due to graphene integration provide alternative routes for current extraction. These resistances are: contact resistance between graphene-AlInP semiconductor (R_{g-w}), graphene sheet resistance (R_g) and contact resistance between graphene-AuGe/Ni/Au (R_{g-m}).

Looking at Figure 6.2, the usual resistances responsible of this lateral series resistance are identified in black. These are the sheet resistance of the front metal (R_m), the specific front contact resistance (R_{FC}) and the top emitter sheet resistance ($R_{E \text{ top Sheet}}$). This last one, is influenced by the AlInP window (R_w) and emitter sheet resistance (R_e). Table 6.1 summarizes the typical values of these parameters.

Table 6.1: Value of the typical resistances participating on the lateral series resistance without the graphene integration on top of the TJSC structure.

Parameter	Value
$R_{m \text{ sheet}}$	0.2-0.4 (Ω/sq)
R_{FC}	$1 \cdot 10^{-5} - 5 \cdot 10^{-5} (\Omega \cdot \text{cm}^2)$
$R_{E \text{ Top Sheet}} (R_{emitter} + R_{window})$	350-500 (Ω/sq)

After graphene integration, new additional resistances (Figure 6.2b, red circles) must be considered since they also participate in the current extraction. According to Figure 6.2 b, graphene sheet resistance (R_g), graphene/front metal resistance (R_{g-m}) and graphene/AlInP window resistance (R_{g-w}) should be analyzed.

In order to assess the role of each current extraction mechanism, a batch of experiments were performed (named as Configuration A and Configuration B). Since graphene sheet resistance was already studied in Chapter 5, we have been focused on the impact of the graphene-front metal contact resistance and the graphene-AlInP window contact resistance. The first ad-hoc structure used for this analysis is Configuration A which is described in *Figure 6.3*. After the thermal evaporation of AuGe/Ni/Au on top of a piece of semi-insulating GaAs substrate, a CVD graphene monolayer was transferred covering half of the metallization and the semi-insulating GaAs substrate. Afterwards, an additional metallization step was used to contact on top of graphene by means of Ti/Pd/Au since we knew from previous TLM measurements performed in Chapter 5, that it produces with ohmic contacts without any thermal treatment.

Figure 6.3: Schematics of configuration A used for the analysis of contact resistance between graphene and the front grid metallization of AuGe/Ni/Au (01_left) and between graphene and Ti/Pd/Au metallization (02_right). Black arrows indicate the contacts used for current injection.

Figure 6.4: I-V curves between the AuGe/Ni/Au – graphene- TiPdAu described in Configuration A_01 and between TiPdAu- graphene- TiPdAu described for Configuration A_02. For both configurations, ohmic contacts are obtained.

If we analyze ConfigurationA_01, the current path available between these two contacts is just graphene, since it is placed on top of a semi-insulating substrate. For ConfigurationA_02, current flows again via the graphene monolayer between the two Ti/Pd/Au metal contacts. In both configurations, the I-V curve presents an ohmic behavior. As it was previously presented in Chapter 5, TiPdAu is frequently used when contacting graphene resulting in ohmic contacts. Additionally, AuGe/Ni/Au resulted in a satisfactory ohmic behavior as well.

In order to evaluate the resistance between graphene-AlInP window layer (R_{g-w}), Configuration B was manufactured. The structure of Configuration B is based on a TJSC structure. The typical AuGe/Ni/Au front grid metallization was deposited in a corner on top of the heavily doped GaAs cap layer to ensure ohmic contacts (its corresponding front contact resistance is the already known, R_{FC}). The rest of the cap layer was chemically etched with $NH_4:H_2O_2:H_2O$ (2:1:10). In order to avoid further oxidation of the AlInP window layer, a graphene monolayer was immediately transferred on top of the structure without touching the front grid metallization already described. Finally, Ti/Pd/Au was deposited both on top of graphene and on top of a small area of the AlInP window layer (Figure 6.5).

Figure 6.5: Sketch of sample B used for the analysis of contact resistance between graphene and the AlInP window layer.

Figure 6.6 shows the measured I-V curves. For the first configuration (Configuration B_01), current flows between the AuGe/Ni/Au (through R_{FC}) front contact and the Ti/Pd/Au contacts via the AlInP window layer (through $R_{TiPdAu/AlInP}$) and the GaInP emitter (through $R_{top\ emitter}$). Since the contact between Ti/Pd/Au/AlInP window is not ohmic, the resulting I-V curve shows a rectifying behavior. For Configuration B_02, current flows both through the Ti/Pd/Au/graphene contact ($R_{TiPdAu/G}$) and through the Ti/Pd/Au/AlInP ($R_{M/AlInP}$) contact via the graphene-AlInP-GaInP emitter pad ($R_{top\ emitter}$ and $R_{G/AlInP}$). The corresponding I-V curve presents a worst behavior,

which indicates that the contact resistance between Ti/Pd/Au-graphene-AlInP presents a worse behavior than the front grid metallization (AuGe/Ni/Au)-Cap-AlInP. Looking at Configuration B_03, the current flows now through the Ti/Pd/Au-graphene contacts ($R_{\text{TiPdAu/G}}$) and through the AuGe/Ni/Au metallization (R_{FC}) via the graphene-AlInP-GaInP ($R_{\text{G/AlInP}}$) top emitter layers ($R_{\text{top emitter}}$). The resistance reduction from the I-V curves can be observed (green curve). This is a consequence of the improvement between the Ti/Pd/Au/AlInP contact by the integration of the graphene layer at the interface. All these experiments reveal that there is actually a current flow between graphene and the AlInP window emitter. On the other hand, the resistance between these two layers is not negligible and thus it needs to be considered and reduced.

Figure 6.6: I-V curves for the three configurations B-01(dark curve), B-02 (red) and B-03 (green curve) shown in Figure 6.5 (left). The same I-V curves presented in semi-logarithmic (right)

Table 6.2: Summary of the electrical contacts obtained at the different interfaces of each configuration

<i>Graphene/TiPdAu</i>	<i>Graphene/AuGe/Ni/Au</i>	<i>Graphene/AlInP</i>
Ohmic contacts	Ohmic contacts	Schottky contacts

According to these results, we can conclude that the highest resistance between graphene and any of the neighbouring layers (AuGe/Ni/Au, Ti/Pd/Au or AlInP) is at the graphene/AlInP window layer since a Schottky behavior had been shown between these two layers.

6.2.3. Graphene – AlInP interface

Following with the graphene integration on a TJSC and the new paths that might participate on the photocurrent extraction, the most critical one has been found to be the contact resistance between the graphene monolayer and the n-type AlInP window layer.

The band alignment between these two materials (graphene/AlInP) will depend on its Fermi level position. The work function was already studied in Chapter 5. With the help of UPS measurements, we detected the direct influence of the substrate where graphene is deposited (SiO₂/Si, AlInP, AuGe/Ni/Au...) on graphene's work function. Additionally, it has been found in the literature, that when graphene is placed in contact with a semiconductor layer, the graphene/semiconductor junction properties seem to be strongly dependent on the fabrication technique with variations from sample to sample [Di Bartolomeo 2016]. That is why the band alignment between these two materials needs to be analyzed for our particular case. Moreover, the doping level achieved in the AlInP window layer will be also a key factor in relation with the conduction mechanism dominating at this interface.

6.2.3.1. Band alignment between graphene and AlInP window layer.

When graphene is placed in contact with a semiconductor, a strong Van der Waals attraction exists, and at the same time, a Schottky barrier at the interface is formed [Jie et al. 2013, Li et al. 2015, Li et al. 2010, Tongay et al. 2009]. In conventional metal –semiconductor interfaces, upon the application of a voltage bias, due to the high density of states at the Fermi level (E_F) it remains constant. However, due to the low density of states at the graphene monolayer, Raman measurements have revealed that graphene's Fermi level is altered during the charge transfer with the semiconductor layer [Chiu et al. 2011, Tobin et al. 1988].

When the semiconductor electron affinity (χ_e) is smaller than the work function of graphene (Φ_G), the Schottky barrier height (Φ_b) created at the interface can be described by Eq. 6.1 for n-type AlInP. In order to be able to study the energy band diagram between graphene and the AlInP window layer, Φ_G was obtained by UPS measurements as already described in Chapter 5. Theoretically, the AlInP electron affinity is ~ 3.78 eV [Gudovskikh et al. 2008]. The energy bandgap of the AlInP window layer used in this thesis is in the order of 2.34-2.36eV. The graphene's work function on top of this AlInP window layer resulted in a value of ~ 4.86 eV without pre-cleaning of the surface and ~ 4.95 eV after a cleaning treatment with Argon (Ar) (already described in Chapter 5). Notice how both values of the graphene work function are higher than the theoretical value of ~ 4.6 eV (when the E_F level is at the Dirac point) [Takahashi et al. 1985]. This difference is attributed to the already studied high p-type doping as result of the CVD graphene transfer by the wet transfer method (Chapter 5). Thus, from these extracted values the barrier height obtained was between 0.82-1.17eV (see Table 6.3). Since we are not completely sure about the direct influence of this pre-cleaning with Ar at the graphene/AlInP interface, we decided to analyze both experimental results graphene/AlInP work function with and without pre-cleaning (4.95eV and 4.86eV respectively) together with the theoretical graphene work function

of 4.6eV. No work regarding graphene/AlInP junction has been found in the literature while graphene/Si and graphene/GaAs junctions are widely studied. Some parameters regarding these junctions have been summarized in Table 6.3. Additionally, the presence of a very thin oxide layer at the graphene/semiconductor surface may affect the barrier height [Tongay et al. 2009].

Although theoretical analysis have presented how the work function is reduced as long as the number of graphene monolayers is increased (and thus, sheet resistance is reduced) [Lin et al. 2013], to start with in this work, graphene work function has been just analyzed for one graphene monolayer.

$$\Phi_b = \Phi_G - \chi_e \quad \text{Eq. 6.1}$$

Figure 6.7: Schematic energy diagram of graphene and AlInP before they are physically connected with their corresponding work functions (Φ_{AlInP} , Φ_G). For graphene (left), the valence band is filled with electrons up to the Fermi level (E_F). The energy difference between Fermi energy and vacuum level corresponds to the graphene work function. For the n-type AlInP semiconductor (right), the energy difference between the vacuum level and the conduction band corresponds to the electron affinity (~ 3.78 eV). The conduction band (C.B) and the valence band (V.B) are separated by the energy bandgap of ~ 2.35 eV. The position of the Fermi level (thus, AlInP work function) is influenced by the doping level.

Table 6.3: Graphene work function for pristine graphene (E_F at the Dirac point), for graphene/Si junctions, graphene/GaAs junctions, graphene/4H-SiC junctions and for the experimental value obtained for graphene transferred on top of the AlInP window layer in this thesis. The work function of G/AlInP layer was measured prior and after the G/AlInP surface pre-cleaning with Argon.

	Ar pre-cleaning of the surface	Φ_G (eV)	χ_{sc}	Φ_{barrier} (eV)
Theoretical(pristine graphene)	—	4.6[Takahashi et al. 1985]	—	—
G/Si n-type ($\sim 4 \cdot 10^{15} \text{ cm}^{-3}$)	—	4.91 [Chiu et al. 2011]	4.05eV	0.86
G/GaAs n-type ($\sim 3.5 \cdot 10^{16} \text{ cm}^{-3}$)	—	4.89 [Chiu et al. 2011]	4.10eV	0.79
Graphene/4H-SiC n-type	—	[Sonde et al. 2009]	3.70eV	0.85
G/AlInP n-type ($\sim 3 \cdot 10^{19} \text{ cm}^{-3}$)	No	4.86 in this work	3.78eV	1.08
G/AlInP n-type ($\sim 3 \cdot 10^{19} \text{ cm}^{-3}$)	Yes	4.95 in this work	3.78eV	1.17

Since the doping level of the semiconductor where graphene is in contact with (in this particular case the AlInP window layer) plays an important role, simulations of the band alignment are essential in order to study the impact on the current extraction mechanisms. For this purpose, we have carried out simulations¹⁴ with Silvaco Atlas TCAD modeling tool [Software.D.S 2015]. In order to evaluate the graphene integration on a TJSC, a conventional TJSC structure with an AlInP window layer of $\sim 40\text{nm}$ was used. Additionally, as the first simple approach for these simulations, graphene was considered as an electrode with a specific work function (*Figure 6.8*) Since simulations are 1D, neither lateral conduction nor metal grid losses are taken into account. Besides, they do not influence the current conduction mechanisms at the graphene/AlInP Schottky contact that we want to determine (by thermionic emission or by tunneling) [Matsuzawa et al. 2000].

Figure 6.8: Scheme of the semiconductor structure analyzed in the simulations. The ohmic contact at the back metallization (not shown) and the Schottky contact on top (between graphene and AlInP window layer) were established as boundary conditions.

Moreover, since these TJSC structures are targeted to work at high concentrations, the doping level of the AlInP window layer is intended to be high. As it was already mentioned in Chapter 3, this can be accomplished with the use of Se and Te as dopants [Dai et al. 2015]. In this line, when doping densities higher than 10^{19} cm^{-3} are achieved in the AlInP window layer, the current is able to spread through relieving the emitter from high current densities [Ochoa et al. 2016]. Accordingly, we have measured the carrier concentration in the AlInP window layer by Electrochemical Capacitance-Voltage (ECV). The carrier concentration in the AlInP window layers analyzed was in the range of $\sim 2 \cdot 10^{19} - 3 \cdot 10^{19}\text{ cm}^{-3}$. Once, both graphene's work function and AlInP doping concentration were experimentally evaluated, simulations of the band alignment were performed for the TJSC structure described in *Figure 6.8* by varying these two

¹⁴Simulations performed by Mario Ochoa

parameters. Graphene's work function was varied from 3.78 eV - 4.95eV. This range was chosen to simulate from the desirable value of 3.78eV (equal to the AlInP affinity) to 4.95eV which was experimentally measured by UPS. Additionally, this range contains the theoretical graphene's work function of 4.6eV. Regarding the AlInP doping values, they were varied from 10^{18}cm^{-3} to 10^{20}cm^{-3} .

Figure 6.9: Energy band alignment at equilibrium for a graphene monolayer (with an experimental work function of 4.86eV) and an AlInP window layer as function of its doping level.

Figure 6.9 illustrates the band alignment at equilibrium for a graphene monolayer (i.e., with a work function of 4.86eV) in contact with an AlInP window layer as a function of its doping level. The Schottky barrier height formed for this particular case is $\sim 1.08\text{eV}$ (Table 6.3). As it can be observed in the figure, as the doping level of the AlInP window layer is increased, the Schottky barrier width is reduced and the possibility of tunneling starts to be significant.

Furthermore, simulations of the corresponding dark J-V curves (Figure 6.10) were carried out taking into account the influence of both thermionic emission and tunneling mechanisms. The different colors correspond to a specific AlInP doping level as a function of the graphene Φ_G range presented (3.78, 4.86 and 4.95eV).

Figure 6.10: Simulated dark I-V curves showing the influence of both thermionic emission and tunneling mechanisms as a function of the experimental graphene work function 4.86eV (dashed), 4.95eV (solid) and the ideal 3.78eV (squares) for several AlInP doping levels ($1 \cdot 10^{18}$, $1.5 \cdot 10^{18}$, $3 \cdot 10^{18}$, $5 \cdot 10^{18}$, $7 \cdot 10^{18}$ and $>1 \cdot 10^{19}$ cm^{-3}). Different equivalent concentration levels (1-1000suns) are highlighted in current density axis when considering a J_{SC} of $\sim 14\text{-}15 \text{ mA/cm}^2$ at 1 sun.

On the one hand, it is important to remark that if tunneling is not considered in these simulations, thermionic emission is not able to extract the carriers at this interface (not shown). On the contrary, for each AlInP doping level and for the three graphene work functions shown, tunneling appears as the dominating mechanism, being its influence higher as the doping level is increased. Additionally, from these plots we can determine the best situation that would occur if the graphene work function was equal to the AlInP electron affinity ($\chi_{AlInP} \sim 3.78 \text{ eV}$) where an ideal ohmic behavior is achieved (black square dots). The value of graphene work function starts to have an impact at different current density levels as a function of the AlInP doping level. As an example, graphene's work function influence appears for J_{SC} of $\sim 2000 \text{ mA/cm}^2$ when the AlInP layer presents a doping level of $7 \cdot 10^{18} \text{ cm}^{-3}$ while such influence appears for J_{SC} of $\sim 80 \text{ mA/cm}^2$ for a lower AlInP doping level of $5 \cdot 10^{18} \text{ cm}^{-3}$. It is interesting to note that when the AlInP doping level is increased over 10^{19} cm^{-3} , the dark J-V curves related to the tunneling mechanism follow an ideal J-V curve behavior for the whole voltage range studied (2-3.5V), being the impact of graphene work function less pronounced. Since the maximum doping level achieved for the AlInP window layer of our solar cells is in the range of $2 \cdot 10^{19}$ - $3 \cdot 10^{19} \text{ cm}^{-3}$, we may consider this situation as the

most real case. As a result of these preliminary simulations, when the AlInP doping level is $\geq 1 \cdot 10^{19} \text{cm}^{-3}$, the tunneling mechanism is the one responsible for the carrier transport at this interface. Additionally, tunneling is more significant as the AlInP doping level is increased.

After all these simulations, graphene work function as well as AlInP doping level have demonstrated to be key factors. On the one hand, if we were able to tune graphene work function to energy levels of 3.78eV (as for example by changing graphene carrier concentration to n-type doping levels by using chemical doping), tunneling limitations due to the AlInP window doping level would no longer exist. On the other hand, as the AlInP window doping layer is increased – higher than 10^{19}cm^{-3} – the tunneling mechanism dominating the current extraction in this graphene/AlInP interface will not be limiting when working at very high currents, since it behaves as an ohmic contact with negligible specific contact resistance. If very high doping levels are achieved, we can also consider a very interesting design regarding the front grid metallization. This new design will consist only on the bus bar metallization without any finger grids (and thus reducing the shadowing factor). In that way, graphene will be transferred on top of both bus bar and the active area of the solar cell (with the heavily doped AlInP window layer). Accordingly, since a 3% in photocurrent will be gained due to the suppression of front metal grid (which results in a ~3% of shadowing factor) the use of several graphene layers with their corresponding absorption and also their corresponding sheet resistance needs to be further analyzed for this new design. All these interesting results, are out of the scope of this Thesis and will be analyzed in the future.

6.3. Graphene integration into a triple junction solar cell

6.3.1. Introduction

The transfer of CVD graphene monolayers on top of the MJSC structures was carried out by the wet transfer method already described in Chapter 5. Different processing steps need to be performed to have a complete TJSC integrating graphene (graphene transfer, mesa etching definition, encapsulation...).

At the beginning of this thesis, for some solar cell structures, graphene monolayers were deposited by an outsourced company. Thus, different processing steps were carried out over a long period of time between them which is not desirable in order to preserve both graphene and the solar cell quality. As a negative example, the cap layer removal needs to be done at IES lab

prior to sending the samples to the outsourced company for graphene deposition. This step leaves the window layer of AlInP in contact with the atmosphere for several days/weeks until graphene is transferred at the company. Such prolonged exposure could further degrade the interface between graphene/AlInP. As long as the AlInP window surface is oxidized, graphene potential to extract the photogenerated current at this interface will be diminished.

Moreover, once graphene has been deposited, a lot of time passed until samples are received back at IES, which makes that all the steps participating in this transfer and processing suffer from lack of repeatability. Again, special care should be paid on graphene detachment. That is why we have done thermal treatments of $\sim 120^{\circ}\text{C}$ of 30 min in most of the processing steps (shown in the following section).

At the same time, special attention is paid to preserve both the front and back metallization, which are already evaporated when graphene is going to be transferred. This means that the thermal annealing at 350°C during 2-3h in H_2 - which is intentionally done in order to further reduce the amount of PMMA residues (Chapter 5) - needs to be reduced down to $\sim 200^{\circ}\text{C}$ to preserve the metallization quality.

Furthermore, in order to isolate each solar cell, mesa etching is needed. Following the TLMs mesa etching isolation for samples containing graphene (Chapter 5), a RIE step is required as a dry method to etch graphene.

All these difficulties, lack of control and requisites presented during the transfer of CVD graphene on top of our MJSC structures, reinforced the idea of developing a graphene transfer process in our lab at IES-UPM, to consequently reduce the amount of time and obstacles between each step.

6.3.2. Graphene transfer at IES-UPM

TJSC analyzed in this section correspond to lattice matched GaInP/Ga(In)As/Ge TJSC solar cells grown by MOVPE provided by a company (IQE). These solar cells were processed in our lab following our conventional processing steps. The way of analyzing the effect of graphene integration in the solar cell performance is described in this section.

The whole processing involving photolithography steps, metal evaporation by joule effect and rapid thermal annealing treatments (RTA) was performed on a piece of semiconductor wafer. After the definition of the front and back metallization, the cap layer was chemically removed

and graphene was immediately deposited on half of the semiconductor piece. Therefore, solar cells from the same epiwafer, with the same manufacturing processing, and with and without graphene could be compared.

Table 6.4: Brief summary of the different wet transfer steps for a monolayer of CVD-graphene on solar cells samples.

<i>Steps</i>	<i>Time</i>
<i>PMMA coating (2500rpm) on top of graphene/Cu</i>	1 min
<i>Baking step 130°C</i>	10-15 min
<i>Cu etching with FeCl₃</i>	30 min
<i>3 water steps</i>	5 min
<i>HCl:H₂O (1:3)</i>	5 min
<i>3 water steps</i>	5 min
<i>Graphene scooped and transferred onto a desired substrate (i.e., solar cells sample)</i>	
<i>Drying consciously with N₂</i>	2 min
<i>Baking at 80°C</i>	15 min
<i>Baking at 120°C</i>	15 min
<i>Rinse in acetone</i>	>2h
<i>Methanol + dry with N₂</i>	2 min
<i>Thermal treatment 200°C sccm H₂ or H₂+Ar ~200sccm</i>	3h

Graphene transfer was performed following the wet transfer steps described in Chapter 5, excepting the reduction of the final thermal treatment down to 200°C for 3 hours in order to avoid degradation of the already deposited metal contacts (back and front contacts). For this thesis, CVD graphene/Cu samples were cut in ~ 1x1 cm² pieces. Table 6.4 summarizes the different wet transfer steps:

Please note that for a sample containing a second graphene monolayer, all these steps were repeated again as described in Table 6.4. Moreover, it should be pointed out, that for these samples, as a final step, an Al layer of ~1.5nm was deposited by thermal evaporation in order to protect graphene monoatomic layers from the subsequent photolithography steps.

6.3.3. Characterization of the graphene transfer on solar cells

Even if graphene characterization by rudimentary techniques such as optical microscope is not simple, it can give us important information about the transfer, such as graphene cracks or dust particles, graphene detachment or even the detection between each graphene layer. Since graphene has been transferred in half of the epiwafer, graphene edges are quite easy to identify as

the amount of dust particles being accumulated in that regions is higher, making easier the delimitation.

Moreover, we have used Atomic Force Microscope (AFM) working in tapping mode to try to identify how good the graphene adherence is and how good the accommodation is on the whole solar cell since it is not a flat surface due to the presence of the front metallization (bus bars and fingers).

With this two simple techniques (optical microscope and AFM), we try to confirm the satisfactory graphene transfer on top of the solar cells.

6.3.3.1. Optical Microscope characterization

Looking at the optical image from *Figure 6.11b*, during the graphene transfer process, the identification of the graphene monolayer can be easily recognized in some of the steps (i.e., when PMMA resist on top of graphene has not been removed yet). On the contrary, after PMMA removal, the optical image of the whole epiwafer reveals that the detection of the already deposited graphene monolayer is not so clear (*Figure 6.11a*).

Figure 6.11: a) Optical microscope image of the TJSC epiwafer after the evaporation of the front contact metallization and graphene transfer. It can be observed from the optical image a variety of the typical devices defined with the usual photolithography mask (solar cell structures together with some test devices such as TLMS, diodes, Van der Pauw structures, etc.). b) Optical microscope image after the graphene/PMMA deposition on top of a TJSC sample.

By using the graphene edges as guides to the eye (*Figure 6.12*), we can determine the solar cell structures that actually contain graphene on top of them. The same procedure is followed when a second graphene monolayer wants to be identified (*Figure 6.13*). Moreover, what these optical images reveal is the clean surface obtained after graphene transfer. Even if the accumulation of dust particles between one and two graphene monolayers might be increased, a clean surface after the second graphene monolayer deposition can be still observed (*Figure 6.13*).

Figure 6.12: Optical microscope image of a graphene monolayer transferred on top of some solar cells. Since graphene identification by optical microscope is difficult, the edges of the graphene monolayer are used as guide to the eye for graphene delineation (left). Magnification of a solar cell containing one graphene monolayer (1MLG). A clean surface can be observed (right).

Figure 6.13: Optical microscope image of the second graphene layer transferred on top of some solar cells. The edge of the second graphene layer provides the identification between one and two monolayer region of the solar cell (left). Magnification of a solar cell containing two graphene layers (2MLG). Even if the accumulation of dust particles between one and two graphene monolayers might be increased, a clean surface after the second graphene monolayer deposition can be still appreciated (right).

As it was described in Chapter 5, graphene detachment used to happen when longtime passed between each step, and when no thermal treatment was performed prior to critical steps such as photoresist deposition at some photolithography step such as RIE or mesa etching. Again, the use of the optical microscope after each step may help us identify several problems such as graphene detachment (*Figure 6.14*).

Figure 6.14: Optical microscope image of graphene detachment after the removal of the photoresist used for the RIE step. No thermal treatment was performed prior to the photoresist deposition.

6.3.3.2. Atomic force microscope characterization

Following with the morphological characterization, AFM scans in tapping mode were performed on the solar cells with graphene. Since the distance between fingers and between fingers and busbar is much higher than the nominal finger width ($\sim 3\mu\text{m}$), we would expect that graphene monolayer will follow the morphology of the solar cell in a satisfactory way.

Figure 6.15 a) shows example of an AFM scan on a metal finger covered by graphene. The finger width obtained was around $\sim 3.5\text{nm}$. From these results we can confirm that graphene adherence between each finger and the solar cell active region is reasonable. Moreover, Figure 6.15 b) shows the AFM scan of the busbar and active area. An abrupt step between busbar and active area can be observed indicating a suitable graphene adherence to the solar cell surface.

Figure 6.15: AFM topography scans with the Z-scale scan of the front metallization of a TJSC containing one graphene monolayer. a) Finger with graphene on top ($\sim 3.5\mu\text{m}$ width). b) Busbar and the active area with graphene on top.

From these results, we can conclude that graphene adherence to the solar cell top surface (active area and its front metallization) is very satisfactory, being most of the solar cell completely covered with graphene.

6.3.4. Reactive Ion Etching (RIE) of graphene for the solar cell mesa isolation

One of the last steps concerning the usual processing of the solar cell devices is the already mentioned mesa etching. The typical mesa etching at IES-UPM is based on a series of wet chemical etchings that selectively etch each semiconductor layer until the Ge wafer is reached in order to electrically isolate the devices. Since graphene is chemically inert to these wet etchings and it is placed at the top of the semiconductor layers, this chemical etching will not be effective until graphene is removed from the mesa area. We have used a dry etching based in an oxygen plasma namely, a reactive ion etching (RIE) to remove graphene from these areas. In Chapter 5 the typical range of parameters used for RIE was studied. In this particular case a value of 8 sccm of O_2 at 100W for 30-40 seconds was found good enough for the graphene etching. Using again the optical microscope, we could identify the etched graphene regions (see *Figure 6.16b*).

Figure 6.16: a) Optical microscope image of a TJSC epiwafer covered with one graphene monolayer prior to RIE. b) Optical image magnification after the graphene RIE at the required areas.

Since there was not a specific RIE mask available for this graphene step, the photolithography mask used for the RIE etching step, was the same that will be used for the following mesa etching. In that way, we avoid graphene to suffer another photolithographic step that will involve cleaning

of the photoresist used for the RIE step and consequently, a second deposition of photoresist + photolithography for the mesa etching.

Figure 6.17: Sketch of the steps performed for the isolation of each individual solar cell after graphene transfer. a) Graphene on top of the solar cell. b) Graphene RIE on top of the mesa area ($\sim 75\mu\text{m}$ width). c) Final mesa after the chemical etching of each semiconductor layer until the Ge substrate is reached.

Figure 6.17 describes this process in three main stages. Because of the photomask characteristics, graphene layer covers the whole solar cell area, namely both active and metallization regions (see *Figure 6.17 c*). We have also considered the idea of different mask designs (i.e., graphene on the whole active area and at the same time covering half of the bus bar or just graphene on the whole active area). In order to evaluate the best option, several batches of samples with different masks designs are required. Due to the lack of time within the frame of this thesis, this work is proposed for the future.

On the other hand, the solar cell encapsulation based on: a) individual sawing of each solar cell with the use of a dicing saw, b) encapsulation of each solar cell on a copper substrate (back contact) with In paint and finally, c) front contacts made on a Printed Circuit Board (PCB) to the bus bar devices by wire bonding with Al/Si wires of $\sim 33\mu\text{m}$ of diameter, was carried out.

Figure 6.18: a) Encapsulation of 1mm^2 GaInP/Ga(In)As/Ge TJSCs incorporating one monolayer of CVD graphene on top. b) Magnification of the solar cell with the bonding wires.

The presence of graphene on the busbar, did not produce any inconvenient when doing the wire bonding. Due to the ultrasonic force applied during the bonding step, we think that wires are in intimate contact with both graphene and the busbar metallization.

Summarizing, in this section we have presented the complete procedure for the integration of graphene in a TJSC by using the wet transfer method. Different manufacturing steps were analyzed and slightly modified in order to avoid both graphene and metallization degradation. At the same time, optical microscopy together with AFM were demonstrated as very useful techniques for the control of the graphene condition in each step.

6.4. Electro-optical characterization of TJSCs with graphene

6.4.1. Introduction

Once described the integration of graphene in our TJSCs, we proceeded with the evaluation of the optical and electrical effects of such graphene incorporation. As previously mentioned, for a more equitable analysis, the comparison will be always carried out for TJSCs with and without graphene from to the same epiwafer and fabricated in the same batch. This comparison has been carried out on solar cells without antireflection coating layers (ARC). Nevertheless, a brief study of the EQE of TJSCs with graphene incorporating also ARC will be presented at the end of this section.

6.4.2. EQE measurements

TJSCs with graphene were evaluated in terms of their external quantum efficiency (EQE). Since we have demonstrated along Chapter 5 and 6 that graphene might be affected by several factors (such as CVD growth and different steps during the wet transfer process), EQE was performed on different devices as summarized in *Figure 6.19*. TJSCs without graphene have been plotted in red, TJSCs with one graphene monolayer in blue and TJSCs with two graphene monolayers in green. *Figure 6.19 a)* presents the EQE of solar cells with an active area of 1mm^2 and without finger metallization (no shadowing factor). Short-circuit current density was calculated from the convolution of the EQE with the reference spectrum (AM1.5d ASTM G173-03 normalized to 1000 W/m^2). For the TJSC without graphene, $J_{sc} \sim 11.03\text{mA/cm}^2$ for the GaInP top cell while $J_{sc} \sim 10.46$ for the Ga(In)As middle cell (*Figure 6.19 a)*). The current mismatch factor obtained (CM_{middle}^{top}) between these subcells (without ARC) is ~ 0.95 . The integration of 1MLG on top of

the TJSC provides a J_{SC} similar for both the GaInP and Ga(In)As subcells. As it was expected, the J_{SC} obtained for the TJSC integrating two graphene monolayer is slightly lower (a relative 2% lower for the top cell).

Figure 6.19 b) shows the EQE of similar solar cells (from the same epiwafer) but now with front grid metallization fingers (with a shadowing factor $\sim 3\%$) that will be used in the concentration measurements below. It should be pointed out, that shadowing due to the metal fingers will result in a lower EQE. Looking at the EQE, a J_{SC} loss of 0.6% at the GaInP TC was calculated for the TJSC integrating graphene and 1.94% for the TJSC integrating 2 graphene monolayers. Besides, a variation in the resonant oscillations can be appreciated for the middle subcell response between TJSC with and without graphene for both EQE in figures *a)* and *b)*.

In order to discard graphene as the main responsible for the change in these oscillations, additional TJSCs without graphene were fabricated from two different regions of the wafer separated 1cm between each other (*Figure 6.19 c)*). As it can be observed, a similar shift is obtained although graphene is not present, which reveals that the dispersion in layer thickness across the wafer (which might be related to a variation of a few nanometers in the thickness of the GaInP top cell) is the main cause responsible for the oscillation shift. Additionally, simulations of the EQE middle subcell of a TJSC with graphene of different thicknesses were performed with Silvaco-Atlas in order to detect these oscillation shifts. As it can be observed from *Figure 6.19 d)*, an EQE decrease as graphene thickness is increased, while no oscillation shift is appreciated.

Moreover, graphene integration may contribute to the AlInP window layer passivation, slowing down its oxidation rate since graphene has been found to serve as a diffusion barrier to oxygen and water molecules [Bunch et al. 2008, Chen et al. 2011, Lange et al. 2011]. Looking at the EQE measurements of *Figure 6.19 a)* for the blue wavelength range (AlInP window spectral response) it seems that the EQE is slightly better for both TJSC integrating one and two graphene monolayers. However, this was not observed for the rest of the EQE measurements (i.e., *Figure 6.19 b)*). In order to shed light on this fact, EQE simulations of the GaInP subcell with different surface recombination velocities (SRV) at the top AlInP window layer (40nm in thickness) were performed. As can be seen in *Figure 6.19 f)* a low impact of SRV is found for these specific AlInP window properties. However, if thinner window layers were used (i.e., 20nm in thickness) a higher impact of the surface recombination velocity is shown by simulations. Thus, graphene passivation effect should not be discarded in the future since it might have some impact depending on the AlInP window properties. However, this interesting effect could be also masked by small differences in the EQE (from 300-350nm wavelength) related to a slight variation of the AlInP window layer thickness (1-5nm). Moreover, processing steps such as selective etching of the

contact layer (from 20-60s) might be behind this effect, since reflectance ($R(\lambda)$) variations at this energy range had been observed in our group after the contact layer removal.

Figure 6.19: a) Experimental EQE of GaInP and Ga(In)As subcells of a TJSC without graphene (red circles), with one graphene monolayer (blue circles) and with two graphene monolayers (green circles) with an active area of 1mm² and no front metal fingers. b) Experimental EQE of similar devices as in a) but with 9 metal fingers that will be used for the concentration measurements. For the solar cells of figure a and b, CVD graphene was grown and transferred at MIT. c) Experimental EQE of the Ga(In)As subcell of two TJSCs from the same wafer separated 1cm. No graphene was deposited on these devices. d) EQE simulations of the Ga(In)As subcell for different graphene thickness. e) Experimental EQE of the GaInP and Ga(In)As subcells of a TJSC without graphene (red circles), with one graphene monolayer (blue circles) and with two graphene monolayer. CVD graphene grown by an external company and transferred at IES-UPM. f) Simulations of the GaInP EQE without graphene as a function of surface recombination velocity (SRV) at the top of AlInP window layer. No ARC was deposited on the solar cells.

Finally, CVD graphene grown by Graphenea, was transferred at IES-UPM onto solar cells in order to compare the impact of a different CVD graphene on the EQE. The area of these solar cells is around $0.5 \times 0.5 \text{ cm}$ which allows at the same time to deposit a larger graphene layer directly on top of the solar cell area. In this case, graphene was deposited on half of the solar cell area. With this configuration, EQE can be measured at different regions of the solar cell, with and without graphene, in order to check the reproducibility along the wafer. Reproducibility was confirmed and as it can be observed in *Figure 6.19 e*, the expected behavior is obtained for one and two graphene monolayers (namely, a slight decrease of EQE of both TC and MC as graphene monolayers are deposited). For this particular case, a J_{SC} decrease of 1.8% and 3.8% was achieved at the GaInP TC for one and two graphene monolayers, respectively. For the GaInAs middle cell, a decrease of 0.6% and 2.2% was obtained when one and two graphene monolayers were deposited.

As conclusion of this subsection, it should be pointed out that the EQE variations due to graphene integration vary between each graphene fabrication and transfer steps (a J_{SC} decrease of 0.5-1.8% for 1MLG and 2-3.8% for 2MLG). However, we can confirm that graphene integration does not affect in a very detrimental way the spectral response of the TJSC.

6.4.3. Dark I-V measurements

To continue with the electro-optical characterization, dark I-V curves were measured on solar cells of 1 mm^2 with 9 metal fingers already analyzed with EQE measurements (*Figure 6.19 b*). Considering the I-V curves from *Figure 6.20*, we can confirm that graphene integration does not affect the recombination mechanisms, since no substantial change can be observed. Indeed, dark I-V curves with and without graphene present two similar slopes related to J_{01} and J_{02} saturation currents. Any additional difference is associated with the expected statistical variability from cell to cell. Additionally, no changes in the series resistance are observed. This is expected since dark I-V curves mainly detect vertical series resistance, which indicates that graphene does not affect it.

Figure 6.20: Dark I-V curve of triple-junction solar cells without graphene (red dots), with one graphene monolayer (blue dots) and with two graphene monolayers (green dots). These solar cells are the same used for the EQE measurements from Figure 6.19 b with an active area of 1mm².

6.4.4. Light I-V measurements

Figure 6.21 shows the I-V curve of these triple junction solar cells with and without graphene under a concentration of 548 suns (54.8 W/cm²). Fill factor (FF) at that irradiance level reaches ~ 85.5% without graphene and it is increased up to 87.6% and 88.0% for one and two graphene monolayers, respectively. On the contrary, the decrease of J_{SC} is of 0.14A/cm² (TJSC_1MLG) and 0.19A/cm² (TJSC_2MLG) due to graphene absorption. Such decrease in current is around 2.3% for one monolayer graphene and around 3.0% for two graphene monolayers which is close to the absorption values obtained for mono and bilayer graphene in Chapter 5. On the other hand, V_{OC} experiences almost no change. These interesting results suggest that the influence of graphene may help to reduce the lateral series resistance and increase the fill factor, with the slightly better result of the FF for two monolayers graphene as a result of the lower sheet resistance (see Chapter 5). However, at the same time losses in the photocurrent are present. This reduction in photocurrent should be counterbalanced by the improvement in the FF at higher concentrations. Thus, I-V curves at different irradiance levels have been analyzed in the following section.

Figure 6.21: Illumination I-V curve of triple junction solar cells without graphene (red dots), with one graphene monolayer (blue dots) and with two graphene monolayers (green dots) under an irradiance of 548 $\times$.

6.4.5. Concentration measurements

Concentration measurements were performed with the use of a flash lamp. For a detailed explanation of the concentration set-up, the flash lamp and its potential, the reader is referred again to [Domínguez 2012].

Interesting results of these subcell limiting diagrams can be obtained for our particular study. On the one hand, analyzing Figure 6.22, when no graphene is present on these triple junction solar cells, the subcell limiting diagram indicates that the TC is slightly limiting since at SMR=1, the normalized photocurrent at the top cell is a bit lower than the normalized photocurrent at the middle cell (Figure 6.22 A). In particular, the CM_{middle}^{top} is ~ 0.98 . On the other hand, when one or two graphene monolayers are deposited on the triple junction solar cells, the subcell diagram indicates that the normalized photocurrents of both TC and MC are slightly decreased. This photocurrent decrease is especially prominent at the middle cell (in consistence with their corresponding EQE measurements from Figure 6.19 b). Since the TJSC without graphene was TC-limited (for the isotypes used in these concentration measurements), this effect observed with graphene ends up by evening out the photocurrents of both TC and MC subcells, thus increasing the current matching between them ($CM_{middle}^{top} \sim 0.99$ for graphene-based TJSC).

Figure 6.22: Subcell limitation diagram of the TC and MC of TJSC without graphene (A), with one graphene monolayer (B) and with two graphene monolayers (C).

Coming back to EQE measurements (section 6.4.2) where the middle cell was limiting the whole photocurrent instead of the top cell resulting in the concentration measurements, we have to consider the influence of possible differences on the spectral response (intensity variations or during the wavelength range) between our DUT and the isotypes cells or reference cell used in each case. Since both top and middle subcells are quite close in photocurrent, the use of different reference cells for a particular measurement (EQE or flash) could result in a change in which subcell is limiting. Even so, what is observed is the slight decrease in I_{SC} for TJSCs with graphene.

In order to study the influence of graphene integration in our TJSC, all the concentration measurements that will be shown in the following plots were performed by searching $SMR=1$ at each concentration level. In such way, we ensure that the measurements are performed at an equivalent AM 1.5d spectrum.

As it was expected, short circuit current is directly proportional to the irradiance level. Figure 6.23 confirms how I_{SC} increases linearly with light intensity. The aforementioned reduction in photocurrent due to the presence of one and two graphene monolayers is summarized in Table 6.5.

Figure 6.23: Short circuit current (I_{sc}) versus irradiance level ($\times$) for TJSC without graphene (red squares), TJSC with one graphene monolayer (1MLG, blue squares) and TJSC with two graphene monolayers (2MLG, green squares).

According to this linear dependence, I_{sc} at 1sun has been calculated with the use of Eq. 6.2, where $C(1)$ is the irradiance level at one sun, and $C(\times_i)$ the irradiance level at i suns.

$$I_{sc}(1\times) = \frac{I_{sc}(i)}{C(\times_i)} \cdot C(1) \quad \text{Eq. 6.2}$$

Due to minimum variations at each concentration measurement, I_{sc} average is presented in Table 6.5 for the three types of solar cells (without graphene, 1MLG and 2MLG). The I_{sc} decrease has been also calculated.

Table 6.5: I_{sc} average at 1 sun from the I_{sc} values obtained at different concentrations. Additionally, the relative losses are also calculated.

TJSC	I_{sc} at $1\times$ (mA)	Relative I_{sc} losses
Without graphene	(0.115 ± 0.001)	—
1MLG	(0.113 ± 0.001)	1.7%
2MLG	(0.112 ± 0.001)	2.6%

Figure 6.22 shows the fill factor (FF) as a function of concentration. As a very interesting result, it can be observed a clear improvement of FF when graphene is integrated on the solar cell. At low concentration levels, FF values are almost the same for cells with and without graphene. FF

differences are greater for concentrations $> 430\times$ when the current density starts to be high enough so that the negative effect of the series resistance cannot be neglected. As concentration increases, the differences in FF further increase.

Figure 6.24: Fill factor (FF) versus concentration for TJSC without graphene (red squares), TJSC with one graphene monolayer (1MLG, blue squares) and TJSC with two graphene monolayers (2MLG, green squares). TJSC without ARC layers.

Relative differences of 4.1% from a TJSC without graphene to a TJSC with one graphene monolayer are achieved. It should be pointed out, that no clear differences are observed between the use of one and two graphene layers. Although further experiments need to be carried out to explain this fact, these interesting results confirm the suitability of integrating graphene on top of the TJSC to extract the photogenerated current in a more efficient way.

Looking at the V_{OC} dependence with concentration, *Figure 6.25* shows the performance of TJSCs with and without graphene. As an interesting result, a slightly higher V_{OC} of 7-10mV is achieved for solar cells with graphene. This could be explained in terms of the series resistance reduction [Algora et al. 2016.]. This is in agreement with the FF improvement for solar cells with graphene thanks also to a series resistance reduction. However, the difference is not higher when concentration levels are further increased. Thus, we cannot discard a possible sample variation as the mechanism behind this fact. To confirm these results future experiments will be performed.

Figure 6.25: Open circuit voltage (V_{oc}) versus irradiance level (X) for TJSC without graphene (red squares), TJSC with one monolayer graphene (1MLG, blue squares) and TJSC with two monolayers graphene (2MLG, green squares).

As a last step, in order to see how all these parameters affect the performance of the TJSC with and without graphene, the efficiency is calculated as a function of concentration. Since the efficiency of a solar cell is defined as the ratio between the output power from the solar cell and the input power (P_{in}) impinging the solar cell, Eq. 6.3 was used.

$$\eta = \frac{FF \cdot V_{oc} \cdot I_{sc}}{P_{in} \cdot A_c} = \frac{FF \cdot V_{oc} \cdot I_{sc}}{(C) \cdot E_{AM.1.5D} \cdot A_c} \quad Eq. 6.3$$

Looking at Eq. 6.3, we should consider that FF and V_{oc} are improved with the use of graphene, but at the same time, the short circuit current is slightly decreased (at least for the graphene deposited on these solar cells). In order to see an improvement in the efficiency, a positive balance of these effects is required. As a result, FF and V_{oc} improvements needs to override the I_{sc} losses due to the presence of graphene. This is what is actually observed at high concentrations (emphasized arrows of Figure 6.26). Only for such high concentrations, the efficiency of TJSC integrating graphene exceeds the efficiency of a TJSC without graphene (red squares are below green and blue squares). As an example, for an irradiance level of $\sim 945\times$, an absolute improvement of 2.3% of the efficiency with respect to TJSC without graphene was achieved with one monolayer graphene and 1.6% for TJSC with two graphene monolayers. On the other hand, due to the limitations of our flash set-up, the study of this evolution at even higher concentrations levels could not be performed. Even if an exact value of the efficiency improvement cannot be obtained from these results, a satisfactory enhancement of the graphene-based solar cells

efficiency can be observed. When working at high concentrations, the efficiency of graphene-based TJSC surpass that of solar cells without graphene confirming the potential of graphene for its use in MJSC at very high concentrations levels (i.e., $> 1000 \times$).

Figure 6.26: Efficiency (η) versus concentration ($\times$) for TJSC without graphene (red squares), TJSC with one graphene monolayer (1MLG, blue squares) and TJSC with two graphene monolayers (2MLG, green squares). Blue and green arrows indicate the positive evolution of the efficiency of the TJSC with one and two graphene monolayers at high concentrations with respect to the efficiency evolution of the TJSC without graphene (red arrow). Efficiency values are low because the solar cells do not have an ARC.

To conclude with these concentration measurements, the value of series resistance (r_s) is estimated. As can be seen in Figure 6.26, efficiency starts to decrease at high concentrations since the photogenerated current density that need to laterally flow along the emitter, grid fingers and busbar is much higher and the voltage drop due to series resistances becomes increasingly significant. The power loss is proportional to the square of the current (I^2R), thus power losses due to series resistance increase as the square of the concentration.

In order to quantify the series resistance, Eq. 6.3 was used as an approximation [Coello et al. 2004]. E is defined as the irradiance for 1 sun (1000W/m^2) and A_c the solar cell area. Looking at Table 6.6, from the calculated series resistance, even if the estimated value is quite high, it can be appreciated how it is mitigated with the use of graphene (being slightly better for one graphene monolayer).

$$r_s = -\frac{d\eta}{dc} \frac{EA_c}{I_{sc}(1)^2} \quad \text{Eq. 6.3}$$

Table 6.6: Summary of the series resistance (r_s) calculated from the fit at high concentrations with the use of Eq. 6.3. Mitigation of series resistance due to the presence of graphene can be appreciated.

TJSC	$r_s (\Omega)$
Without G	~ 3.4
1MLG	~ 1.3

To the best of our knowledge, little work can be found in the literature related to graphene incorporation on III-V MJSC to enhance its efficiency as a transparent electrode [Chang et al. 2013]. In that paper, concentration measurements of graphene based MJSC are presented. However, remarkable differences exist with our approach. On the one hand, graphene synthesis is performed by Inductively coupled plasma-enhanced chemical vapor deposition (ICP-CVD) by using a Si/SiO₂/Ni substrate, where no precise control of the number of graphene monolayers can be carried out, which has been demonstrated to be an important parameter to be considered. In that way, no control of graphene monolayers as well as no control of the complete coverage with graphene of the active area of the solar cell is taken into account. On the other hand, several considerations such as AlInP doping level concentration and the different thermal treatments performed along the different steps are not presented.

6.4.6. Spatially resolved electroluminescence measurements

As a powerful technique, electroluminescence (EL) was used to further confirm graphene contribution to the lateral current flow. EL is a straightforward tool that is used to evaluate the performance of a TJSC (front grid design, front grid defects such as broken fingers, epitaxial defects at each subcell and so on) [Duggan et al. 2009, Kong et al. 2015].

When forward biasing solar cells they behave such as LEDs (see Figure 6.27). We have used a current injection of 50 mA and 100mA to emulate their behavior at high concentration levels, namely, $\sim 450\times$ and $\sim 900\times$, respectively (assuming $J_{SC}^{1\times} \sim 10\text{-}11\text{mA/cm}^2$ without ARC). The emitted light is recorded with a CCD camera (CCi4 MV1-D1312I Photon Focus). In order to segregate the GaInP emission (650-690nm) a short pass filter is used (cut off wavelength 800nm). On the contrary, a long pass filter (cut on wavelength 800nm) was used for the Ga(In)As middle cell which has an emission around $\sim 870\text{nm}$. At the same time, macroscopic and some microscopic defects in the semiconductor structure can be also identified with this method, since they will appear as dark spots in the EL image.

Figure 6.27: TJSC emitting under a specific forward voltage.

The electroluminescence images investigated in this work were the produced only by the GaInP top and Ga(In)As middle subcells, since the bottom cell (BC) is made of Ge (indirect bandgap) which produces a very low signal requiring an expensive detector unavailable in our lab.

In order to complement these EL measurements, simulations with the 3D distributed model¹⁵ [Galiana 2006], were carried out to emulate the EL behavior of both GaInP and GaInAs subcells and to estimate important parameters such as the graphene/AlInP contact resistance.

For a better visualization of these results, *Figure 6.28* and *Figure 6.29* present the color maps of the GaInP and GaInAs subcells emission (normalized EL intensity) for both experimental and simulated response.

On the one hand, a non-uniform voltage distribution can be observed for the two kind of TJSC devices (without graphene and with one monolayer graphene) at the GaInP top cell (*Figure 6.28*). As expected, the highest EL intensity appears near the busbar where the current is injected through the wires bonded on the bus. The injected current flows laterally via metal grid and GaInP emitter. Since lateral series resistance at the top layers (AlInP window and GaInP emitter) is not negligible, lateral current distribution will vary accordingly. On the other hand, as it can be observed, a slight decrease of this lateral series resistance is achieved when graphene is integrated, which results in a more homogeneous current distribution (*Figure 6.28* left). This effect can be appreciated with a lower variation of the EL intensity from the perimeter of the active area to the center (i.e., more homogeneous voltage distribution). Similar behavior is achieved for the EL simulations (*Figure 6.28* right). Different simulation parameters were varied in order to achieve the best fit. For this particular case, graphene sheet resistance was varied between 100-800Ω/sq.

¹⁵ 3D simulations performed by Iván Lombardero

The best fit was obtained for a value of $\sim 200\Omega/\text{sq}$. Additionally, the estimation of the specific contact resistance between graphene and the AlInP window layer was in the order of $\sim 10^{-2}\Omega/\text{cm}^2$.

Figure 6.28: Experimental (left) and simulated (right) false color maps of electroluminescence of the GaInP subcell of a TJSC with and without graphene at a forward current of 100mA. The top metallization of these TJSC has 9 grid fingers. Solar cell area: 1mm^2 . Experimental false color maps show emission at the fingers together with a lower signal close to the busbar (in red) than can be attributed to a lambert emission detected by the EL camera that is not considered in the simulation.

In a similar way, EL emission was recorded for the GaInAs subcell (*Figure 6.29* left). Alike the GaInP EL emissions already described, GaInAs EL emissions resulted in a slight improvement of the current distribution when graphene is integrated on the TJSC. However, it must be noted that the main enhancement is obtained for the GaInP subcell where graphene is contacting. Again, a good fit was achieved in (*Figure 6.29* right). In summary, we can confirm the positive effect of graphene to the contribution of lateral current spreading in a more uniform way all along the active area. As already remarked, since the contact resistance between graphene and the AlInP window is not fully optimized by now, we might expect an even more uniform distribution once this resistance is reduced.

Figure 6.29: Experimental (left) and simulated (right) false color maps of electroluminescence (normalized EL intensity) of the GaInAs subcell of a TJSC with and without graphene at a forward current of 100mA. The top metallization of these TJSC has 9 grid fingers. Solar cell area: 1mm².

With the aim of reducing the contact resistance between graphene and the surface of interest (metal or semiconductor), the substitution of Van der Waals binding energies between these interfaces by covalent bonds should be investigated. Once graphene monolayers have been deposited on top of the multijunction solar cell, patterning graphene might enhance the formation of covalent bonds between the surface of interest and graphene etch sites. As an example of patterning we could consider the exposition of certain areas of graphene to O₂ plasma in order to etch graphene in a specific pattern. Thus, assisted by the promotion of covalent bonds, the reduction of contact resistance between these interfaces will result in a more efficient performance when integrating graphene on these multijunction solar cells [Na et al. 2017]. However, this study is out of the scope of this thesis and all these preliminary results reinforce the idea of graphene potential in combination with concentrator solar cells.

6.4.7. Antireflecting coating layers for TJSC with graphene

Antireflective coating layers (ARC) consist of a few nanometers of dielectric materials with refractive index between air and semiconductor materials ($1 < n_{\text{ARC layer}} < 3$) that are used to minimize optical losses due to reflection of the impinging light onto the semiconductor structure. At the same time, the materials and thickness used in the ARC system should be optimized in order to produce the highest J_{SC} of the TJSC by means of the most suitable current matching among the subcells. ZnS/MgF₂ is the typical ARC stack used at IES-UPM (similar to the ARC presented in Chapter 4). Due to the lack of time, no specific ARC optimization work was done on TJSC with graphene during this thesis. On the other hand, since the reflectance of the AlInP window layer did not exhibit a significant change when graphene was deposited on top (Chapter 5), we assumed as a first approach the use of our already established ZnS/MgF₂ ARC system. With all these considerations, deposition of ARC layers on TJSC with graphene was briefly studied.

6.4.7.1. ARC deposition

Typical ARC layers used at IES-UPM are based on ZnS/MgF₂ stack with thicknesses of ~ 40 - 50 nm for the ZnS and ~ 80 - 100 nm for MgF₂. For the pertinent characterization of TJSCs with and without graphene, the same ARC thicknesses were used (50nm ZnS and 100nm MgF₂). ARC layers were deposited by e-gun deposition.

Figure 6.30: Optical image of a TJSC after the deposition of ZnS/ MgF₂ ARC. Left image corresponds to a TJSC without graphene, while the right image corresponds to a TJSC with one graphene monolayer. Inhomogeneities can be observed after the ARC deposition for the solar cell with graphene.

Regarding TJSCs with graphene, after the ARC evaporation, we realized that the aspect was different from previous homogeneous ARC layers achieved for TJSC without graphene (*Figure 6.30* left). There were some inhomogeneities that may be due to the interaction between graphene,

possible water molecules or dust particles with the ARC layers during the evaporation step (Figure 6.30 right).

In order to suppress or mitigate these inhomogeneities, a thermal treatment prior to the ARC deposition was considered again. An annealing of 120°C for 30 min in nitrogen (N_2) was carried out. Accordingly, TJSC containing graphene after this thermal step were immediately placed in vacuum inside the ARC evaporation chamber.

Figure 6.31: EQE of the GaInP top cell of a TJSC with one graphene monolayer. EQEs of the two GaInP subcells with graphene are almost identical before the ARC deposition. After the ARC deposition, it can be observed that EQE is better for the GaInP subcell where a thermal treatment had been performed prior to the ARC deposition (empty blue circles).

The EQE of these solar cells was measured before and after the ARC deposition. The EQE of the GaInP subcell was almost identical for both TJSCs with graphene prior to the ARC coating. As it can be observed in Figure 6.31, it seems that this thermal treatment may be beneficial to ensure a better ARC deposition for solar cells with graphene, thus enabling an improved spectral response. This better performance for the GaInP subcell, has been observed for several solar cells, although further experiments regarding these thermal treatments are ongoing to explore and optimize the best treatment. Additionally, we should point out the presence of such inhomogeneities is still visible under the optical microscope after ARC deposition on samples where the thermal treatment had been carried out.

To finish this section, Figure 6.32 shows the EQEs of representative TJSCs without graphene (red circles) and with one graphene monolayer (blue circles) both having the same ARCs.

Although some inhomogeneities in the ARC are present at the surface, preliminary EQE results confirm the good behavior of these conventional ARC layers on TJSC with graphene since a similar response and a similar J_{sc} (i.e., $J_{sc,TC}^{without\ graphene} \sim 14.4\text{ mA/cm}^2$ and $J_{sc,TC}^{with\ 1MLG\ graphene} \sim 14.2\text{ mA/cm}^2$) are obtained.

Figure 6.32: EQE of the GaInP, Ga(In)As and Ge subcells of the TJSC without graphene (red dots) and with one graphene monolayer (blue dots). Both solar cells have the same ARC system (50nm ZnS and 100nm MgF₂).

Summarizing, in this section we have demonstrated that the ARC deposition technology existing at IES-UPM could be satisfactorily used for TJSC with graphene. Nevertheless, further investigations about optimized ARC layers for TJSC with graphene must be accomplished in order to achieve the maximum efficiency of these solar cells.

6.5. Summary and conclusions

In this chapter, the integration of CVD graphene on lattice matched GaInP/Ga(In)As/Ge triple junction solar cells has been carried out for the first time at IES-UPM. The integration of graphene consists in its deposition on the solar cell top surface (active area + front metallization). With this approach, lateral series resistances are positively affected by the presence of graphene, which allows extra paths for current flow.

During the study of these new current paths, the most critical one has been found to be the contact resistance between graphene and the n-type AlInP window layer. On the one hand, p-type

doping of CVD graphene transferred by the wet transfer method (Chapter 5) increases graphene's work function from the theoretical value of 4.6eV up to values of 4.86-4.95eV. Differences on the work function between graphene and the AlInP neighboring layer result in a non-optimized interface with the formation of a Schottky barrier, which needs to be reduced. On the other hand, due to the high doping level values achieved at the AlInP window layer ($2\text{-}3 \cdot 10^{19} \text{ cm}^{-3}$) tunneling between graphene and the AlInP window layer allows the current to flow between these two layers. Moreover, simulations with Silvaco Atlas reinforce the need of increasing the doping level of the AlInP window layer to even higher doping values ($\geq 3 \cdot 10^{19} \text{ cm}^{-3}$) so tunneling mechanism will be governing the photocurrent extraction at even higher current densities (i.e., higher concentration levels). In addition, n-type doping of graphene (work function reduction) will also contribute to reduce the Schottky barrier formed at the graphene-AlInP interface.

Triple-junction solar cells were fabricated following the conventional processing steps carried out in our group. Front and back metallizations were deposited prior to graphene transfer. CVD graphene monolayers (from MIT and from Graphenea) were used. Additionally, in order to have most of the fabricating steps in our hands, the graphene wet transfer process was performed at IES-UPM lab with satisfactory results (preserving both the graphene and the TJSC quality).

The evaluation of the graphene integration onto the TJSC epiwafers was carried out by analyzing the performance of solar cells from the same epitaxial wafer without graphene and with one and two graphene layers. EQE shows almost the same behavior for these devices with and without graphene although a very slight J_{sc} loss is observed. To confirm its effectiveness at high illumination levels, light I-V curves at different concentrations were studied. The main result is the improvement of the FF at concentration levels $> 500\times$ for the TSJC with graphene which is an unequivocal proof of the reduction of the lateral series resistance. An absolute improvement of 3.5% in FF at $\sim 760\times$ have been achieved. This series resistance reduction was also confirmed by electroluminescence (both experimental and simulated) where a more uniform current distribution on the GaInP top cell was observed for the solar cells with graphene. In summary, TJSCs with graphene show a small loss in J_{sc} as a consequence of the non-negligible absorption of graphene, which is counterbalanced by a better FF caused by a lower series resistance. When concentration is further increased the efficiency of TJSC with graphene outperforms the efficiency of the solar cells without graphene. All these facts confirm the potential of graphene for its use in MJSC especially at ultra-high concentrations ($> 1000\times$).

Finally, antireflection coating layers were briefly analyzed. The conventional ZnS/MgF₂ ARC design used in our group was applied on the TJSC with graphene as an initial approach. The same ARC thicknesses were deposited on TJSC with and without graphene. Although further

experiments should be carried out in the future, the spectral response achieved for the cells with graphene is at the same level of the spectral response achieved for TJSC without graphene, which confirms the suitability of these ARCs for TJSC with graphene.

All these results confirm the potential of CVD graphene, with exceptional optical and electrical properties, to further enhance the efficiency of MJSC especially at ultra-high concentrations.

Chapter 7

SUMMARY, CONCLUSIONS AND FUTURE WORK

7.1. Introduction

The aim of this final Chapter is to point out the main challenges and conclusions reached during this thesis as well as different aspects and work to be addressed in a near future. Thus, each of the following sections is related to one of the chapters presented in this document (from Chapter 2 to Chapter 6, except from the Introduction which is Chapter 1 and the present Chapter 7).

7.2. Effect of Ge autodoping during III-V on Ge epitaxy by MOVPE

Both Ge solid-phase diffusion and gas-phase Ge autodoping have been demonstrated to play an important role when growing GaInP and Ga(In)As layers on Ge substrates by MOVPE. The minimum thickness of the GaInP nucleation and GaInAs buffer layers to withhold the diffusion from the Ge wafer and prevent it from reaching the active layers of the MJSC device was evaluated. For the critical case of growing a very thin GaInP nucleation layer of 50nm, a Ga(In)As

buffer layer with a thickness of 230nm has been shown to be thick enough to withhold the Ge solid-phase diffusion (for our specific reactor geometry and growth parameters). Moreover, growth parameters such as temperature and V/III ratio have been found to directly influence the Ge autodoping in GaInP and Ga(In)As layers grown on Ge wafers. On the contrary, growth rate (at a given V/III ratio) seems to have a lower influence on Ge autodoping. Additionally, Ga(In)As is more affected than GaInP by Ge autodoping (a factor 2 and 3 for V/III ratios of ~ 65 and ~ 130 respectively) which could be attributed to a higher partial pressure of Ge present in the gas phase as a result of a more severe Ge substrate etching when AsH_3 is used (as compared to PH_3). However, due to morphological requisites higher V/III ratios are used when growing GaInP layers than for Ga(In)As, which in practice makes stronger the effect of unwanted Ge incorporation in the GaInP top cell. We also found that the conditions and coatings in the reactor prior to growth had an influence on Ge autodoping. For example, an initial coating based on GaAs and GaInP was found to getter Ge atoms. To complete this study, Ge autodoping was also evaluated as a function of wafer size and it was found to be more severe in larger wafers, suggesting that it is an area-driven phenomenon. Finally, with the use of a Si_3N_4 backside coating on the Ge wafer, Ge autodoping was mitigated.

As a result of these findings, the following works may be pursued in the future:

- In section 2.2.3, we measured a lower Ge concentration in III-V semiconductor layers grown at lower V/III ratios. This encourages us to study new routes for growing GaInP layers (such as the GaInP nucleation layer and the GaInP top cell) at lower V/III ratios. This is not an easy task since, in our MOVPE reactor, better morphologies, lower roughness and lower density of defects are obtained for GaInP layers grown at higher V/III ratios. Thus, the trade-off between lower Ge contamination and good morphology will need to be optimized.
- In section 2.2.4, the important role of the growth temperature was demonstrated in Ge autodoping. This indicates that the temperature used to grow GaInP and Ga(In)As layers, which is in the range of 640-675°C in a TJSC, could be further decreased. A growth temperature of $\sim 600^\circ\text{C}$ will be explored in the near future.
- The performance of selected GaInP TCs –with the same EQE but containing different amount of Ge contaminant– is also a very interesting route in order to understand the overall impact of Ge contamination on the electrical performance of a complete MJSC. Characterization techniques such as photoluminescence (PL), SIMS or deep level

transient spectroscopy (DLTS) will be used since they might provide additional information about electrically active defects and deep levels due to this Ge contamination.

7.3. Towards further development of the triple junction solar cell

The main goal of Chapter 3 was to face three paths to enhance the efficiency of the TJSC. With the aim of mitigating the thermal load on the BC associated with the growth of the complete TJSC structure, a new nucleation routine was developed. An improvement of almost $\sim 50\text{mV}$ (at 500 suns) was demonstrated in the V_{OC} of the Ge subcell by means of the use of a thinner GaInP nucleation layer (50nm at 675°C) and a thinner Ga(In)As buffer layer grown at a lower temperature (500nm at 600°C). Again, Si_3N_4 coatings on the backside of the Ge wafer turned out to be beneficial for the diffusion mechanisms that lead to the formation of the BC emitter. Additionally, the GaInP TC optimization was carried out pursuing two improvements: 1) the improvement of its V_{OC} through a better understanding and control of the ordering effect in the GaInP using surfactant mediated growth with Sb; and 2) the improvement of its J_{SC} through the increase in the transparency of the window layer using strained AlInP layers with a higher Al content and higher doping achieved with the use of Te as a dopant. An effective decrease in the cutoff wavelength in the EQE of the GaInP solar cell (i.e. an increase in the energy bandgap of the GaInP used) has been obtained with the use of Sb during the growth of the GaInP material (both base and emitter regions). In addition, we demonstrated that both the degree of order of the solar cell emitter and base layers influence the shape of the EQE of the devices. To complete this study, TEM measurements were performed on GaInP:Zn samples where different Sb/P ratios had been used during their growth to confirm that, even though the degree of ordering was reduced with the use of Sb, it does not change the type of ordering, which is CuPt_B . Additionally, a slight increase of $\sim 15\text{mV}$ in V_{OC} was estimated when a Sb/P ratio of 728ppm is used during the emitter growth. Regarding the very transparent and conductive high band gap TJ integrated in the complete TJSC, the mitigation of the parasitic junction that was presumably formed between some of the neighboring layers (primarily the GaInP:Si window layer and the GaInAs middle cell emitter) was studied and sorted out by increasing the doping level of the window layer or using the old n-AlGaAs window with a thin n^{++} -GaInP capping layer.

As a result of these findings, the following works may be pursued in the future:

- The degradation observed in the BC V_{OC} after suffering the thermal load of the growth of the complete TJSC structure encouraged us to explore new nucleation routines in order

to mitigate this load. Even though satisfactory results were achieved, the influence of the growth temperature should be further reduced since it plays an important role. For instance, with the reduction of the Ga(In)As growth temperature down to 600°C, the BC V_{oc} was increased (section 3.2.3). Thus, the growth temperature of the GaInP nucleation layer could be also reduced to 600°C in order to mitigate as much as possible such load. At the same time, the trade-off between temperature and good morphology must be taken into account. If good morphology is preserved at this low growth temperature, then the thickness of both GaInP and Ga(In)As layers could be also re-calibrated and possibly further reduced, since at lower temperatures the impact of Ge solid-phase diffusion should be also reduced (shallower Ge diffusion profiles will be achieved). Therefore, thinner layers will be enough to withhold Ge solid-phase diffusion and, besides, growth duration will be reduced.

- Preliminary results show that, the use of a Si_3N_4 backside coating on the Ge wafers seems to influence the diffusion mechanisms that take place during the emitter formation in a positive way (section 3.2.4). A gain of ~10-15mV was obtained. This is a promising result, which is far from being understood and thus further experiments need to be performed.
- With the aim of understanding better the interface problems originated with the incorporation of the new high bandgap TJ, TEM measurements will be performed to assess the integration of the TJ structure in the complete MJSC. Additionally, to complete this study, high band gap TJ devices with different neighboring layers should be processed and characterized with the corresponding I-V curves at low temperature.

7.4. Development and characterization of the improved triple junction solar cell

The implementation of the improvement paths developed along Chapter 3, was carried out in complete TJSCs. Three different TJSC Stages integrating gradual modifications with respect to the Reference TJSC have been presented in Chapter 4. The GaInP TC was further disordered with the use of Sb during the growth of both GaInP emitter and base regions. In addition, the TC was enhanced with the use of a higher doping level (with Te) in the AlInP window as well as a higher Al composition (0.8% higher than the Reference TJSC). The improvement in the EQE of these devices shows the potential of these structures in comparison with the Reference. In particular,

for Stages II and III, a J_{SC} gain at both TC and MC subcells have been measured. Moreover, the BC EQEs are very similar with respect to the Reference and no evident difference stands out after the integration of the new nucleation routine. I-V curve measurements taken on this new batch of TJSC showed a satisfactory performance with a reduction in the recombination current when the new nucleation routine was incorporated. However, when these structures were processed using a similar processing as the one carried out for the Reference (1mm² active area, conventional metallization based on evaporated AuGe/Ni/Au, etc.) an unexpected high recombination current was detected. Concentration measurements confirm a V_{OC} loss of ~30-35mV for this new batch of structures with respect to the Reference. In this way, Stage III, which incorporates the new nucleation routine, was expected to have 50mV more than the Reference. Unfortunately, this was counterbalanced by the aforementioned V_{OC} loss of ~30-35mV detected on these new TJSC batches. Thus, the resulting gain with respect to the Reference was only ~15 mV. With all these facts, preliminary concentration measurements on final devices with ARC layers for both Stages II and III were carried out at IES-UPM. Due to the loss in V_{OC} , the efficiency gain with respect to the Reference was lower than the expected. Efficiency values of 40.04% at ~416× were achieved. As a future work, the different hypotheses presented along this chapter to explain this loss should be tested:

- Spectral EL measurements will be also performed in order to have access to the individual I-V curves of each subcell to know the origin of V_{OC} loss.
- In order to discard the possible influence of the use of Sb during the growth of the emitter, any of the new TJSC designs proposed in this Thesis (maybe Stage I) should be grown without any Sb in the emitter. Also, variations in the amount of Sb introduced during the emitter growth could be explored (from 728ppm to 1400ppm).
- In order to check the possible effect of a general loss in minority carrier lifetimes, the Reference design together with Stage I should be grown in the same batch of MOVPE runs. In this way, reactor conditions would be the same for both structures and their comparison would clarify this issue.
- As an alternative characterization, TEM measurements might provide information about the crystalline quality of these GaInP interfaces (base and emitter) grown with different Sb/P ratios.

- The effective doping of the different layers (in both the Reference cell and the new bath of TJSCs) should be carefully assessed to determine their impact on the recombination current of the neutral regions (J_{01}), and thus on the final V_{OC} of the device.
- Additionally, new devices are being processed with an optimized front metallization developed in a recent Thesis in our group based on Ge/Pd/Ti/Pd/Ag. With this new front grid metallization, a much lower series resistance at high concentration can be achieved and thus a significant efficiency boost is expected.
- If all these future works are successful (understanding of the V_{OC} loss and FF improvement with the new metallization based on Ge/Pd/Ti/Pd/Ag), the expected efficiency could overpass 41%.

7.5. Electro-optical properties of graphene for photovoltaics applications

The main challenge of Chapter 5 is the study of graphene potential to enhance the efficiency of a TJSC by its incorporation as a transparent electrode. Graphene monolayers grown by CVD were transferred by the wet transfer method in order to analyze their optical and electrical properties (Chapter 5). The wet transfer method was studied at MIT during a research stay of the PhD candidate and established later at IES-UPM. In this way, surface preparation of the substrate of interest, graphene transfer process together with subsequent photolithography steps were performed in a row, which highly reduced graphene detachment problems and avoided long idle periods between each process step. Electrical properties of CVD graphene such as sheet resistance values of $\sim 300\text{-}500\Omega/\text{sq}$, mobility values of $\sim 750\text{-}2000(\text{cm}^2\text{V}^{-1}\text{s}^{-1})$ and p-type density level between $1.0 \cdot 10^{12}\text{-}3.2 \cdot 10^{13}\text{cm}^{-2}$ were measured. Additionally, the n and k optical parameters of the real graphene/substrate stack were obtained. The work function of graphene was also measured by UPS (4.95eV and 4.86eV with and without pre-cleaning treatment respectively). This important parameter is related to the final doping level. Since graphene turns out to be p-type after the wet transfer process ($\Phi_G > 4.6\text{eV}$), three different doping mechanisms were studied along this chapter to tune graphene work function and obtain a final n-type doping, which was found not to be an easy task.

The study of graphene was initiated from scratch. When this thesis started, no work regarding graphene had been carried out at the Solar Energy Institute of the Technical University of Madrid.

Accordingly, despite the advances made in this Thesis still many challenges remain open. To name a few, the following new pathways have been identified to improvements to be implemented in a near future in our lab:

- A vast variety of transfer methods offer the possibility of transferring graphene with a good quality. Due to the lack of time of this thesis, only a wet transfer method was explored. Therefore, other transfer methods should be assessed in order to find the method that best fits our goal, that is, the transfer of graphene layer to a MJSC structure preserving both graphene and the MJSC quality. As an example, automatic graphene transfer (which avoids handling skills) or dry transfer mechanisms could be used as an alternative to reduce the amount of PMMA dust particles. All these efforts are needed to diminish the impact of unintentional p-type doping in our CVD graphene samples.
- Annealing treatments have been found an indispensable step to improve graphene quality. Thus, different temperatures as well as durations and atmospheres could be evaluated to get full information of their impact on graphene surface.
- In relation with metal contacts and contacting graphene, pre-cleaning treatments with O₂ plasma should be performed prior to evaporation of the metals to eliminate possible residues from the photoresist and thus reduce the specific contact resistance as much as possible.
- Simulations and evaluation of different metals and thickness should be also accomplished in order to determine the best metallization in terms of contact resistance. At the same time, the suitability of such best metallization should be customized for our particular MJSC application integrating graphene.

Additionally, as an interesting pathway on the graphene field, a large effort must be done in relation to the intentional n-type doping of graphene which has been found to be a difficult task. Different optoelectronic devices and applications might require the use of an n-type graphene, thus new n-type doping alternatives should be explored. In our particular TJSC application, the goal would be to fine tune graphene work function for a better current extraction (better band alignment between graphene/AlInP window of our MJSC).

7.6. Integration of graphene on III-V concentrator solar cells

The integration of CVD graphene on lattice matched triple junction (GaInP/Ga(In)As)Ge solar cells has been carried out for the first time at IES-UPM. Since graphene is deposited on top of both the front grid metallization and the active area of the solar cell, lateral series resistances are affected by the presence of graphene, thus new paths for current flow appear. Special attention was paid on graphene/AlInP window interface where AlInP doping concentration was found to play an important role on the current extraction at this interface. Following with graphene transfer onto the TJSC structures, the optimization of several steps was performed (i.e. an additional RIE step). To determine graphene impact, TJSCs from the same epiwafers and same device manufacturing process with and without graphene were fabricated. The main result is the improvement of both FF and Voc at high concentration levels $> 500\times$ for the TSJC with graphene which is the unequivocal probe of the reduction of the lateral series resistance. An absolute improvement of 3.5% in FF at $\sim 760\times$ have been achieved.

As a result of these findings, we foresee the following actions in our near term research:

- The consideration of an alternative approach consisting in the deposition of graphene under the front grid metallization) is also going to be implemented in a near future. As it was mentioned at the beginning of Chapter 6, this second approach presents the advantage of having to transfer graphene on a flat surface. This design, offers the advantage of ensuring graphene coverage on the whole surface so the planar technology achievements could be used. Moreover, thermal treatments to clean graphene surface from PMMA dust particles will not be limited in temperature by the presence of the front metallization. Thus, thermal treatments in the range of 300-400°C can be performed which will result in a cleaner surface. With this second approach, a specific mask design for the different steps will be also required. As a result of this approach, a patent on III-V semiconductor multijunction solar cells incorporating graphene has been filed.
- Regarding the optimization of the graphene/AlInP interface, which could be considered as the bottleneck of this work, more experiments need to be made. The Schottky barrier height formed after the band alignment between both materials should be reduced as much as possible. On the one hand, graphene work function could be slightly tuned by n-type doping. As previously presented in chapter 5, doping graphene n-type has been found to be an elusive task. Additionally, the increase as high as possible of the AlInP

window doping level -with the help of Te or Se dopants- should be also investigated. Moreover, the move to another window material (with and optimized band alignment with graphene) with a high band gap and high doping level could be also considered as a new alternative.

- Once all of these parameters have been optimized, the new design based on a simple bus bar metallization without finger grids should be carried out. In that way, some short-circuit photocurrent will be gained due to the elimination of the shadowing loss. The impact of several graphene layers with their corresponding absorption as well as their corresponding sheet resistance will be further analyzed and optimized in this new design.
- Even if the conventional ARC used in our group (ZnS/MgF_2) seems to fit well with the graphene-based MJSC structure, optical simulations to find the best ARC are also ongoing.
- Additionally, as a new alternative, CVD graphene with an intrinsic p-type doping could be integrated on a p-n multijunction structure where its potential might result in an even higher efficiency increase with respect to a n-p configuration.

Bibliography

[Ahrenkiel et al. 2001] S. P. Ahrenkiel and M. C. Hanna. "Antiphase-boundary extension in single-variant CuPt–B ordered Ga_{0.47}In_{0.53}As on InP". *Applied Physics Letters*, 2001. **79**(12): p.1781-1782.

[Algora 2007] C. Algora 2007. "Very-High-Concentration Challenges of III-V Multijunction Solar Cells". *Concentrator Photovoltaics*. Ed. by A. Luque and A. Viacheslav (Eds.). Vol. 130. Springer Series in Optical Sciences. Springer Berlin Heidelberg, pp.89-111

[Algora et al. 2000] C. Algora and V. Díaz. "Influence of series resistance on guidelines for manufacture of concentrator p-on-n GaAs solar cells". *Progress in Photovoltaics: Research and Applications*, 2000. **8**(2): p.211-225.

[Algora et al. 2001] C. Algora, E. Ortiz, I. Rey-Stolle, V. Díaz, R. Peña, V. M. Andreev, V. P. Khvostikov and V. D. Rumyantsev. "A GaAs solar cell with an efficiency of 26.2% at 1000 suns and 25.0% at 2000 suns". *IEEE Transactions on Electron Devices*, 2001. **48**(5): p.840-844.

[Algora et al. 2016.] C. Algora and I. Rey-Stolle. 2016. Handbook on Concentrator Photovoltaic Technology. Wiley.

[Andreev et al. 2004] V. Andreev, V. Khvostikov, N. Kalyuzhnyi, S. Titkov, O. Khvostikova and M. Shvarts. "GaAs/Ge heterostructure photovoltaic cells fabricated by a combination of MOCVD and zinc diffusion techniques". *Semiconductors*, 2004. **38**(3): p.355-359.

[Avouris et al. 2012] P. Avouris and C. Dimitrakopoulos. "Graphene: synthesis and applications". *Materials Today*, 2012. **15**(3): p.86-97.

[Bae et al. 2010] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong and S. Iijima. "Roll-to-roll production of 30-inch graphene films for transparent electrodes". *Nat Nano*, 2010. **5**(8): p.574-578.

[Bai et al. 2002] A. Bai, F. Seiji and Y. Kiyoshi 2002. Graphitization of 6H-SiC(000) $\bar{1}$ Surface by Scanning Tunneling Microscopy.

[Balci et al. 2012] O. Balci and C. Kocabas. "Rapid thermal annealing of graphene-metal contact". *Applied Physics Letters*, 2012. **101**(24): p.243105.

[Baraket et al. 2010] M. Baraket, S. G. Walton, Z. Wei, E. H. Lock, J. T. Robinson and P. Sheehan. "Reduction of graphene oxide by electron beam generated plasmas produced in methane/argon mixtures". *Carbon*, 2010. **48**(12): p.3382-3390.

- [Barrigón 2014] E. Barrigón 2014. "Development of GaInP/GaInAs/Ge TRIPLE-junction solar cells for CPV applications". PhD Thesis. Dpto. Electrónica Física. ETSIT-UPM.
- [Barrigón et al. 2016] E. Barrigón, L. Barrutia, M. Ochoa, I. Rey-Stolle and C. Algora. "Effect of Sb on the quantum efficiency of GaInP solar cells". *Progress in Photovoltaics: Research and Applications*, 2016. **24**(8): p.1116-1122.
- [Barrigón et al. 2015] E. Barrigón, L. Barrutia and I. Rey-Stolle. "Optical in situ calibration of Sb for growing disordered GaInP by MOVPE". *Journal of Crystal Growth*, 2015. **426**(Supplement C): p.71-74.
- [Barrigón et al. 2013] 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". *Journal of Crystal Growth*, 2013. **370**: p.173-176.
- [Barrigón et al. 2011] E. Barrigón, B. Galiana and I. Rey-Stolle. "Reflectance anisotropy spectroscopy assessment of the MOVPE nucleation of GaInP on germanium (100)". *Journal of Crystal Growth*, 2011. **315**(1): p.22-27.
- [Barrigón et al. 2014] E. Barrigón, I. García, L. Barrutia, I. Rey-Stolle and C. Algora. "Highly conductive p++-AlGaAs/n++-GaInP tunnel junctions for ultra-high concentrator solar cells". *Progress in Photovoltaics: Research and Applications*, 2014. **22**(4): p.399-404.
- [Barrigón et al. 2017] E. Barrigón, M. Ochoa, I. García, L. Barrutia, C. Algora and I. Rey-Stolle. "Degradation of Ge subcells by thermal load during the growth of multijunction solar cells". *Progress in Photovoltaics: Research and Applications*, 2017: p.n/a-n/a.
- [Barrutia et al. 2015] L. Barrutia, E. Barrigón, L. López-Conesa, J. Rebled, S. Estradé, F. Peiró, I. Rey-Stolle and C. Algora. "On the use of Sb to improve the performance of GaInP subcells of multijunction solar cells". 2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC), 2015.
- [Bellon et al. 1989] P. Bellon, J. P. Chevalier, E. Augarde, J. P. André and G. P. Martin. "Substrate-driven ordering microstructure in $GaxIn_{1-x}P$ alloys". *Journal of Applied Physics*, 1989. **66**(6): p.2388-2394.
- [Bernardi et al. 2013] M. Bernardi, M. Palummo and J. C. Grossman. "Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials". *Nano Letters*, 2013. **13**(8): p.3664-3670.
- [Blake et al. 2009] P. Blake, R. Yang, S. V. Morozov, F. Schedin, L. A. Ponomarenko, A. A. Zhukov, R. R. Nair, I. V. Grigorieva, K. S. Novoselov and A. K. Geim. "Influence of metal contacts and charge inhomogeneity on transport properties of graphene near the neutrality point". *Solid State Communications*, 2009. **149**(27): p.1068-1071.
- [Borgström et al. 2011] M. T. Borgström, J. Wallentin, M. Heurlin, S. Fält, P. Wickert, J. Leene, M. H. Magnusson, K. Deppert and L. Samuelson. "Nanowires With Promise for Photovoltaics". *IEEE Journal of Selected Topics in Quantum Electronics*, 2011. **17**(4): p.1050-1061.
- [Borin Barin et al. 2015] G. Borin Barin, Y. Song, I. de Fátima Gimenez, A. G. Souza Filho, L. S. Barreto and J. Kong. "Optimized graphene transfer: Influence of polymethylmethacrylate (PMMA) layer concentration and baking time on graphene final performance". *Carbon*, 2015. **84**(Supplement C): p.82-90.

- [Boscá et al. 2016] A. Boscá, J. Pedrós, J. Martínez, T. Palacios and F. Calle. "Automatic graphene transfer system for improved material quality and efficiency". *Scientific Reports*, 2016. **6**.
- [Bosi et al. 2011] M. Bosi, G. Attolini, C. Ferrari, C. Frigeri, M. Calicchio, F. Rossi, K. Vad, A. Csik and Z. Zolnai. "Effect of temperature on the mutual diffusion of Ge/GaAs and GaAs/Ge". *Journal of Crystal Growth*, 2011. **318**(1): p.367-371.
- [Brückner et al. 2012] S. Brückner, O. Supplie, E. Barrigón, J. Luczak, P. Kleinschmidt, I. Rey-Stolle, H. Döscher and T. Hannappel. "In situ control of As dimer orientation on Ge (100) surfaces". *Applied Physics Letters*, 2012. **101**(12): p.121602.
- [Bunch et al. 2008] J. S. Bunch, S. S. Verbridge, J. S. Alden, A. M. van der Zande, J. M. Parpia, H. G. Craighead and P. L. McEuen. "Impermeable Atomic Membranes from Graphene Sheets". *Nano Letters*, 2008. **8**(8): p.2458-2462.
- [Capasso et al. 2014] A. Capasso, M. D. Francesco, E. Leoni, T. Dikonimos, F. Buonocore, L. Lancellotti, E. Bobeico, M. S. Sarto, A. Tamburrano, G. D. Bellis and N. Lisi. "Cyclododecane as support material for clean and facile transfer of large-area few-layer graphene". *Applied Physics Letters*, 2014. **105**(11): p.113101.
- [Castro Neto et al. 2009] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim. "The electronic properties of graphene". *Reviews of Modern Physics*, 2009. **81**(1): p.109-162.
- [Centurioni 2005] E. Centurioni. "Generalized matrix method for calculation of internal light energy flux in mixed coherent and incoherent multilayers". *Applied Optics*, 2005. **44**(35): p.7532-7539.
- [Coello et al. 2004] J. Coello, M. Castro, I. Antón, G. Sala and M. A. Vázquez. "Conversion of commercial si solar cells to keep their efficient performance at 15 suns". *Progress in Photovoltaics: Research and Applications*, 2004. **12**(5): p.323-331.
- [Coll et al. 2017] C. Coll, E. Barrigon, L. Lopez-Conesa, J. Rebled, L. Barrutia, I. Rey-Stolle, S. Estrade, C. Algora and F. Peiro. "The effect of Sb-surfactant on GaInP CuPtB type ordering: assessment through dark field TEM and aberration corrected HAADF imaging". *Physical Chemistry Chemical Physics*, 2017. **19**(15): p.9806-9810.
- [Copel et al. 1989] M. Copel, M. C. Reuter, E. Kaxiras and R. M. Tromp. "Surfactants in epitaxial growth". *Physical Review Letters*, 1989. **63**(6): p.632-635.
- [Cui et al. 2013] T. Cui, R. Lv, Z.-H. Huang, S. Chen, Z. Zhang, X. Gan, Y. Jia, X. Li, K. Wang, D. Wu and F. Kang. "Enhanced efficiency of graphene/silicon heterojunction solar cells by molecular doping". *Journal of Materials Chemistry A*, 2013. **1**(18): p.5736-5740.
- [Cha et al. 2014] M.-J. Cha, W. Song, Y. Kim, D. S. Jung, M. W. Jung, S. I. Lee, P. D. Adhikari, K.-S. An and C.-Y. Park. "Long-term air-stable n-type doped graphene by multiple lamination with polyethyleneimine". *RSC Advances*, 2014. **4**(71): p.37849-37853.
- [Cha et al. 2015] S. Cha, M. Cha, S. Lee, J. H. Kang and C. Kim. "Low-Temperature, Dry Transfer-Printing of a Patterned Graphene Monolayer". *Scientific Reports*, 2015. **5**.

[Chang et al. 2013] J. Chang, M.-G. Suh, J. Heo, D. Kim, J. Kim, S.-M. Lee, H.-J. Chung and Y. Kim. "Transparent Graphene Electrodes for Highly Efficient III–V Multijunction Concentrator Solar Cells". *Energy Technology*, 2013. **1**(4): p.283-286.

[Chang et al. 2013] J. Chang, M. G. Suh, J. Heo, D. Kim, J. Kim, S. M. Lee, H. J. Chung and Y. Kim. "Transparent Graphene Electrodes for Highly Efficient III–V Multijunction Concentrator Solar Cells". *Energy Technology*, 2013. **1**(4): p.283-286.

[Chapman et al. 2006] D. C. Chapman, A. D. Howard and G. B. Stringfellow. "Zn enhancement during surfactant-mediated growth of GaInP and GaP". *Journal of Crystal Growth*, 2006. **287**(2): p.647-651.

[Charrier et al. 2002] A. Charrier, A. Coati, T. Argunova, F. Thibaudau, Y. Garreau, R. Pinchaux, I. Forbeaux, J.-M. Debever, M. Sauvage-Simkin and J.-M. Themlin. "Solid-state decomposition of silicon carbide for growing ultra-thin heteroepitaxial graphite films". *Journal of Applied Physics*, 2002. **92**(5): p.2479-2484.

[Chen et al. 2011] C.-C. Chen, M. Aykol, C.-C. Chang, A. F. J. Levi and S. B. Cronin. "Graphene-Silicon Schottky Diodes". *Nano Letters*, 2011. **11**(5): p.1863-1867.

[Chen et al. 2014] J.-J. Chen, J. Meng, D.-P. Yu and Z.-M. Liao. "Fabrication and Electrical Properties of Stacked Graphene Monolayers". *Scientific Reports*, 2014. **4**: p.5065.

[Chen et al. 2007] J. H. Chen, M. Ishigami, C. Jang, D. R. Hines, M. S. Fuhrer and E. D. Williams. "Printed Graphene Circuits". *Advanced Materials*, 2007. **19**(21): p.3623-3627.

[Chen et al. 2008] J. H. Chen, C. Jang, S. Adam, M. S. Fuhrer, E. D. Williams and M. Ishigami. "Charged-impurity scattering in graphene". *Nat Phys*, 2008. **4**(5): p.377-381.

[Chen et al. 2011] S. Chen, L. Brown, M. Levendorf, W. Cai, S.-Y. Ju, J. Edgeworth, X. Li, C. W. Magnuson, A. Velamakanni, R. D. Piner, J. Kang, J. Park and R. S. Ruoff. "Oxidation Resistance of Graphene-Coated Cu and Cu/Ni Alloy". *ACS Nano*, 2011. **5**(2): p.1321-1327.

[Chia et al. 2008] C. Chia, J. Dong, D. Chi, A. Sridhara, A. Wong, M. Suryana, G. Dalapati, S. Chua and S. Lee. "Effects of AlAs interfacial layer on material and optical properties of GaAs/Ge (100) epitaxy". *Applied Physics Letters*, 2008. **92**(14): p.141905.

[Chiu et al. 2011] P. Chiu, S. Wojtczuk, X. Zhang, C. Harris, D. Pulver and M. Timmons. "42.3% efficient InGaP/GaAs/InGaAs concentrators using bifacial epigrowth". 37th IEEE Photovoltaic Specialists Conference (PVSC), 2011: IEEE.

[Cho et al. 2013] C.-Y. Cho, M. Choe, S.-J. Lee, S.-H. Hong, T. Lee, W. Lim, S.-T. Kim and S.-J. Park. "Near-ultraviolet light-emitting diodes with transparent conducting layer of gold-doped multi-layer graphene". *Journal of Applied Physics*, 2013. **113**(11): p.113102.

[Dabrowski et al. 2016] J. Dabrowski, G. Lippert, J. Avila, J. Baringhaus, I. Colambo, Y. S. Dedkov, F. Herziger, G. Lupina, J. Maultzsch, T. Schaffus, T. Schroeder, M. Kot, C. Tegenkamp, D. Vignaud and M. C. Asensio. "Understanding the growth mechanism of graphene on Ge/Si(001) surfaces". *Scientific Reports*, 2016. **6**: p.31639.

[Dai 2002] H. Dai. "Carbon nanotubes: opportunities and challenges". *Surface Science*, 2002. **500**(1): p.218-241.

- [Dai et al. 2015] 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". *Journal of Crystal Growth*, 2015. **413**(Supplement C): p.71-75.
- [Das et al. 2008] A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy, A. K. Geim, A. C. Ferrari and A. K. Sood. "Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor". *Nat Nano*, 2008. **3**(4): p.210-215.
- [Dean et al. 2010] C. R. Dean, A. F. Young, MericI, LeeC, WangL, SorgenfreiS, WatanabeK, TaniguchiT, KimP, K. L. Shepard and HoneJ. "Boron nitride substrates for high-quality graphene electronics". *Nat Nano*, 2010. **5**(10): p.722-726.
- [Derkcas et al. 2012] D. Derkcas, R. Jones-Albertus, F. Suarez and O. Fidaner. "Lattice-matched multijunction solar cells employing a 1 eV GaInNAsSb bottom cell". *Journal of Photonics for Energy*, 2012. **2**(021805): p.1-8.
- [Di Bartolomeo 2016] A. Di Bartolomeo. "Graphene Schottky diodes: An experimental review of the rectifying graphene/semiconductor heterojunction". *Physics Reports*, 2016. **606**(Supplement C): p.1-58.
- [Dimroth et al. 2014] F. Dimroth, M. Grave, P. Beutel, U. Fiedeler, C. Karcher, T. N. Tibbits, E. Oliva, G. Siefer, M. Schachtner and A. Wekkeli. "Wafer bonded four-junction GaInP/GaAs//GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency". *Progress in Photovoltaics: Research and Applications*, 2014. **22**(3): p.277-282.
- [Dimroth et al. 2016] F. Dimroth, T. N. Tibbits, M. Niemeyer, F. Predan, P. Beutel, C. Karcher, E. Oliva, G. Siefer, D. Lackner and P. Fuß-Kailuweit. "Four-junction wafer-bonded concentrator solar cells". *IEEE Journal of Photovoltaics*, 2016. **6**(1): p.343-349.
- [DiVincenzo et al. 1984] D. P. DiVincenzo and E. J. Mele. "Self-consistent effective-mass theory for intralayer screening in graphite intercalation compounds". *Physical Review B*, 1984. **29**(4): p.1685-1694.
- [Domínguez 2012] C. Domínguez 2012. "Optical and electrical characterization of high-concentration photovoltaic systems = Caracterización óptica y eléctrica de sistemas fotovoltaicos de alta concentración". PhD Thesis.Dpto. Electrónica Física. ETSIT-UPM.
- [Du et al. 2008] X. Du, I. Skachko, A. Barker and E. Y. Andrei. "Approaching ballistic transport in suspended graphene". *Nat Nano*, 2008. **3**(8): p.491-495.
- [Duggan et al. 2009] G. Duggan and I. M. Ballard. "Evaluation of competing triple junction concentrator cells by electroluminescence ". *34th IEEE Photovoltaic Specialists Conference (PVSC)*, 2009.
- [Dunlap 1954] W. C. Dunlap. "Diffusion of Impurities in Germanium". *Physical Review*, 1954. **94**(6): p.1531-1540.
- [Ernst et al. 1995] P. Ernst, C. Geng, F. Scholz, H. Schweizer, Y. Zhang and A. Mascarenhas. "Band-gap reduction and valence-band splitting of ordered GaInP₂". *Applied Physics Letters*, 1995. **67**(16): p.2347-2349.

[Espinet 2012] P. Espinet 2012. "Advances in the modeling, characterization and reliability of concentrator multijunction solar cells". PhD Thesis. Electrónica-Física. ESIT-UPM.

[Fan et al. 2011] G. Fan, H. Zhu, K. Wang, J. Wei, X. Li, Q. Shu, N. Guo and D. Wu. "Graphene/Silicon Nanowire Schottky Junction for Enhanced Light Harvesting". *ACS Applied Materials & Interfaces*, 2011. **3**(3): p.721-725.

[Fang et al. 2014] H. Fang, C. Battaglia, C. Carraro, S. Nemsak, B. Ozdol, J. S. Kang, H. A. Bechtel, S. B. Desai, F. Kronast, A. A. Unal, G. Conti, C. Conlon, G. K. Palsson, M. C. Martin, A. M. Minor, C. S. Fadley, E. Yablonovitch, R. Maboudian and A. Javey. "Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides". *Proceedings of the National Academy of Sciences*, 2014. **111**(17): p.6198-6202.

[Fang et al. 2014] W. Fang, A. L. Hsu, Y. Song, A. G. Birdwell, M. Amani, M. Dubey, M. S. Dresselhaus, T. Palacios and J. Kong. "Asymmetric growth of bilayer graphene on copper enclosures using low-pressure chemical vapor deposition". *ACS nano*, 2014. **8**(6): p.6491-6499.

[Farmer et al. 2009] D. B. Farmer, R. Golizadeh-Mojarad, V. Perebeinos, Y.-M. Lin, G. S. Tulevski, J. C. Tsang and P. Avouris. "Chemical Doping and Electron-Hole Conduction Asymmetry in Graphene Devices". *Nano Letters*, 2009. **9**(1): p.388-392.

[Ferrari et al. 2006] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim. "Raman Spectrum of Graphene and Graphene Layers". *Physical Review Letters*, 2006. **97**(18): p.187401.

[Fetzer et al. 2000] C. M. Fetzer, R. T. Lee, J. K. Shurtleff, G. B. Stringfellow, S. M. Lee and T. Y. Seong. "The use of a surfactant (Sb) to induce triple period ordering in GaInP". *Applied Physics Letters*, 2000. **76**(11): p.1440-1442.

[France et al. 2015] R. M. France, J. F. Geisz, I. García, M. A. Steiner, W. E. McMahon, D. J. Friedman, T. E. Moriarty, C. Osterwald, J. Scott Ward, A. Duda, M. Young and W. J. Olavarria. "Quadruple-Junction Inverted Metamorphic Concentrator Devices". *IEEE Journal of Photovoltaics SP*, 2015. **5**(1): p.432.

[Friedman 2010] D. J. Friedman. "Progress and challenges for next-generation high-efficiency multijunction solar cells". *Current Opinion in Solid State and Materials Science*, 2010. **14**(6): p.131-138.

[Friedman et al. 2001] D. J. Friedman and J. M. Olson. "Analysis of Ge junctions for GaInP/GaAs/Ge three-junction solar cells". *Progress in Photovoltaics: Research and Applications*, 2001. **9**(3): p.179-189.

[Galiana 2006] B. Galiana 2006. "Desarrollo de la tecnología de MOVPE para el crecimiento de semiconductores III-V: fabricación de células solares para concentraciones luminosas elevadas". PhD Thesis. Dpto Electrónica Física. ETSIT-UPM.

[Galiana et al. 2008] B. Galiana, I. Rey-Stolle, C. Algora, K. Volz and W. Stolz. "A GaAs metalorganic vapor phase epitaxy growth process to reduce Ge outdiffusion from the Ge substrate". *Applied Physics Letters*, 2008. **92**(15): p.152102.

[Gao 2014] L. Gao. "Probing Electronic Properties of Graphene on the Atomic Scale by Scanning Tunneling Microscopy and Spectroscopy". *Graphene and 2D Materials*, 2014. **1**(1).

- [Gao et al. 2012] L. Gao, W. Ren, H. Xu, L. Jin, Z. Wang, T. Ma, L.-P. Ma, Z. Zhang, Q. Fu, L.-M. Peng, X. Bao and H.-M. Cheng. "Repeated growth and bubbling transfer of graphene with millimetre-size single-crystal grains using platinum". 2012. **3**: p.699.
- [Gao et al. 2011] Y. Gao, H.-L. Yip, K.-S. Chen, K. M. O'Malley, O. Acton, Y. Sun, G. Ting, H. Chen and A. K. Y. Jen. "Surface Doping of Conjugated Polymers by Graphene Oxide and Its Application for Organic Electronic Devices". *Advanced Materials*, 2011. **23**(16): p.1903-1908.
- [García 2010] I. García 2010. "Desarrollo de células solares de doble unión de GaInP/GaAs para concentraciones luminosas elevadas (Development of GaInP/GaAs dual-junction solar cells for high light concentrations)". PhD Thesis. Dpto. Electrónica Física. ETSIT-UPM.
- [García et al. 2012] I. García, I. Rey-Stolle and C. Algora. "Performance analysis of AlGaAs/GaAs tunnel junctions for ultra-high concentration photovoltaics". *Journal of Physics D: Applied Physics*, 2012. **45**(4): p.045101.
- [Garcia et al. 2008] I. Garcia, I. Rey-Stolle, C. Algora, W. Stolz and K. Volz. "Influence of GaInP ordering on the electronic quality of concentrator solar cells". *Journal of Crystal Growth*, 2008. **310**(23): p.5209-5213.
- [García et al. 2007] I. García, I. Rey-Stolle, B. Galiana and C. Algora. "Analysis of tellurium as n-type dopant in GaInP: Doping, diffusion, memory effect and surfactant properties". *Journal of Crystal Growth*, 2007. **298**(Supplement C): p.794-799.
- [García et al. 2009] I. García, I. Rey-Stolle, B. Galiana and C. Algora. "A 32.6% efficient lattice-matched dual-junction solar cell working at 1000 suns". *Applied Physics Letters*, 2009. **94**(5): p.053509.
- [Geim et al. 2007] A. K. Geim and K. S. Novoselov. "The rise of graphene". *Nat Mater*, 2007. **6**(3): p.183-191.
- [Geisz et al. 2012] J. F. Geisz, A. Duda, R. M. France, D. J. Friedman, I. Garcia, W. Olavarria, J. M. Olson, M. A. Steiner, J. S. Ward and M. Young. "Optimization of 3-junction inverted metamorphic solar cells for high-temperature and high-concentration operation". AIP Conference Proceedings, 2012: AIP.
- [Georgakilas et al. 2012] V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim. "Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications". *Chemical Reviews*, 2012. **112**(11): p.6156-6214.
- [Gomyo et al. 1988] A. Gomyo, T. Suzuki and S. Iijima. "Observation of Strong Ordering in GaInP alloy semiconductors". *Physical Review Letters*, 1988. **60**(25): p.2645-2648.
- [Gonzalez et al. 2011] M. Gonzalez, A. Carlin, C. Dohrman, E. Fitzgerald and S. Ringel. "Determination of bandgap states in p-type In_{0.49}Ga_{0.51}P grown on SiGe/Si and GaAs by deep level optical spectroscopy and deep level transient spectroscopy". *Journal of Applied Physics*, 2011. **109**(6): p.063709.
- [Graf et al. 2007] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold and L. Wirtz. "Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene". *Nano Letters*, 2007. **7**(2): p.238-242.

- [Green et al. 2015] M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop. "Solar cell efficiency tables (Version 45)". *Progress in Photovoltaics: Research and Applications*, 2015. **23**(1): p.1-9.
- [Greiner et al. 1984] M. E. Greiner and J. F. Gibbons. "Diffusion of silicon in gallium arsenide using rapid thermal processing: Experiment and model". *Applied Physics Letters*, 1984. **44**(8): p.750-752.
- [Grützmacher et al. 1993] D. Grützmacher, T. Sedgwick, A. Powell, M. Tejjwani, S. Iyer, J. Cotte and F. Cardone. "Ge segregation in SiGe/Si heterostructures and its dependence on deposition technique and growth atmosphere". *Applied physics letters*, 1993. **63**(18): p.2531-2533.
- [GTMResearch 2014] GTMResearch. "Concentrating photovoltaics 2011: technology, costs and markets". *GreenTech Media Market Research Report*, 2014.
- [Gudovskikh et al. 2008] 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". *Thin Solid Films*, 2008. **516**(20): p.6739-6743.
- [Guo et al. 2010] C. X. Guo, H. B. Yang, Z. M. Sheng, Z. S. Lu, Q. L. Song and C. M. Li. "Layered Graphene/Quantum Dots for Photovoltaic Devices". *Angewandte Chemie International Edition*, 2010. **49**(17): p.3014-3017.
- [Gupta et al. 2006] A. Gupta, G. Chen, P. Joshi, S. Tadigadapa and Eklund. "Raman Scattering from High-Frequency Phonons in Supported n-Graphene Layer Films". *Nano Letters*, 2006. **6**(12): p.2667-2673.
- [Guter et al. 2009] W. Guter, J. Schöne, S. P. Philipps, M. Steiner, G. Siefer, A. Wekkeli, E. Welser, E. Oliva, A. W. Bett and F. Dimroth. "Current-matched triple-junction solar cell reaching 41.1% conversion efficiency under concentrated sunlight". *Applied Physics Letters*, 2009. **94**(22): p.223504.
- [Haysom et al. 2015] J. E. Haysom, O. Jafarieh, H. Anis, K. Hinzer and D. Wright. "Learning curve analysis of concentrated photovoltaic systems". *Progress in Photovoltaics: Research and Applications*, 2015. **23**(11): p.1678-1686.
- [Hideo et al. 1988] S. Hideo, A. Chikao, Y. Akio and Y. Masafumi. "Double Heterostructure GaAs Tunnel Junction for a AlGaAs/GaAs Tandem Solar Cell". *Japanese Journal of Applied Physics*, 1988. **27**(2R): p.269.
- [Hou et al. 2013] S. Hou, X. Cai, H. Wu, X. Yu, M. Peng, K. Yan and D. Zou. "Nitrogen-doped graphene for dye-sensitized solar cells and the role of nitrogen states in triiodide reduction". *Energy & Environmental Science*, 2013. **6**(11): p.3356-3362.
- [Hsu et al. 2012] A. Hsu, K. K. Kim, D. Nezich, R. Luo, H. Wang, J. Kong and T. Palacios. "Impact of Short Range Scattering in Graphene Electronics". *4th Graphene International Conference*, 2012.
- [Hsu et al. 2011] A. Hsu, H. Wang, K. K. Kim, J. Kong and PalaciosT. "Impact of Graphene Interface Quality on Contact Resistance and RF Device Performance". *IEEE Electron Device Letters*, 2011. **32**: p.1008–1010.

- [Huang et al. 2014] C.-H. Huang, H.-Y. Lin, C.-W. Huang, Y.-M. Liu, F.-Y. Shih, W.-H. Wang and H.-C. Chui. "Probing substrate influence on graphene by analyzing Raman lineshapes". *Nanoscale Research Letters*, 2014. **9**(1): p.64.
- [Huo et al. 2017] P. Huo, B. Galiana and I. Rey-Stolle. "Comparison of Ti/Pd/Ag, Pd/Ti/Pd/Ag and Pd/Ge/Ti/Pd/Ag contacts to n-type GaAs for electronic devices handling high current densities". *Semiconductor Science and Technology*, 2017. **32**(4).
- [IEO 2005] E. IEO. "Energy Information Administration". *International Energy Outlook*, 2005.
- [Ishigami et al. 2007] M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer and E. D. Williams. "Atomic Structure of Graphene on SiO₂". *Nano Letters*, 2007. **7**(6): p.1643-1648.
- [Ismach et al. 2010] A. Ismach, C. Druzgalski, S. Penwell, A. Schwartzberg, M. Zheng, A. Javey, J. Bokor and Y. Zhang. "Direct Chemical Vapor Deposition of Graphene on Dielectric Surfaces". *Nano Letters*, 2010. **10**(5): p.1542-1548.
- [Jae-Phil et al. 2011] S. Jae-Phil, C. Minhyeok, J. Seong-Ran, S. Dongju, L. Takhee and L. Dong-Seon. "InGa_N-Based p-i-n Solar Cells with Graphene Electrodes". *Applied Physics Express*, 2011. **4**(5): p.052302.
- [Jang et al. 2008] C. Jang, S. Adam, J. H. Chen, E. D. Williams, S. Das Sarma and M. S. Fuhrer. "Tuning the Effective Fine Structure Constant in Graphene: Opposing Effects of Dielectric Screening on Short- and Long-Range Potential Scattering". *Physical Review Letters*, 2008. **101**(14): p.146805.
- [Jeong et al. 2010] H. K. Jeong, K.-j. Kim, S. M. Kim and Y. H. Lee. "Modification of the electronic structures of graphene by viologen". *Chemical Physics Letters*, 2010. **498**(1-3): p.168-171.
- [Jie et al. 2013] W. Jie, F. Zheng and J. Hao. "Graphene/gallium arsenide-based Schottky junction solar cells". *Applied Physics Letters*, 2013. **103**(23): p.233111.
- [Jones-Albertus et al. 2015] R. E. Jones-Albertus, F. S. Arias, M. W. Wiemer, M. J. Sheldon and H. B. Yuen 2015, Pseudomorphic window layer for multijunction solar cells. US8962991 B2.
- [Kang et al. 2012] J. Kang, S. Hwang, J. H. Kim, M. H. Kim, J. Ryu, S. J. Seo, B. H. Hong, M. K. Kim and J.-B. Choi. "Efficient Transfer of Large-Area Graphene Films onto Rigid Substrates by Hot Pressing". *ACS Nano*, 2012. **6**(6): p.5360-5365.
- [Kaplas et al. 2016] T. Kaplas, L. Karvonen, S. Ahmadi, B. Amirsolaimani, S. Mehravar, N. Peyghambarian, K. Kieu, S. Honkanen, H. Lipsanen and Y. Svirko. "Optical characterization of directly deposited graphene on a dielectric substrate". *Optics Express*, 2016. **24**(3): p.2965-2970.
- [Kavanagh et al. 1987] L. Kavanagh and C. W. Magee. "Diffusion of Ge in GaAs at SiO₂-encapsulated Ge-GaAs interfaces". *Canadian Journal of Physics*, 1987. **65**(8): p.987-990.
- [Khan et al. 2014] M. F. Khan, M. Z. Iqbal, M. W. Iqbal and J. Eom. "Improving the electrical properties of graphene layers by chemical doping". *Science and Technology of Advanced Materials*, 2014. **15**(5): p.055004.

- [Kim et al. 2015] S. Kim, P. Zhao, S. Aikawa, E. Einarsson, S. Chiashi and S. Maruyama. "Highly Stable and Tunable n-Type Graphene Field-Effect Transistors with Poly(vinyl alcohol) Films". *ACS Applied Materials & Interfaces*, 2015. **7**(18): p.9702-9708.
- [Kim et al. 2013] S. M. Kim, A. Hsu, Y.-H. Lee, M. Dresselhaus, T. Palacios, K. K. Kim and J. Kong. "The effect of copper pre-cleaning on graphene synthesis". *Nanotechnology*, 2013. **24**(36): p.365602.
- [King et al. 2009] R. R. King, A. Boca, W. Hong, X. Liu, D. Bhusari, D. Larrabee, K. Edmondson, D. Law, C. Fetzer and S. Mesropian. "Band-gap-engineered architectures for high-efficiency multijunction concentrator solar cells". 24th European Photovoltaic Solar Energy Conference and Exhibition, Hamburg, Germany, 2009.
- [Kobayashi et al. 2013] T. Kobayashi, M. Bando, N. Kimura, K. Shimizu, K. Kadono, N. Umezu, K. Miyahara, S. Hayazaki, S. Nagai, Y. Mizuguchi, Y. Murakami and D. Hobara. "Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process". *Applied Physics Letters*, 2013. **102**(2): p.023112.
- [Kobeleva et al. 2013] S. P. Kobeleva, I. M. Anfimov, S. Y. Yurchuk, E. A. Vygovskaya and B. V. Zhalnin. "Influence of $\text{In}_{0.56}\text{Ga}_{0.44}\text{P}/\text{Ge}$ heterostructure on diffusion of phosphorus in germanium during the formation of multiple solar cells". *Technical Physics Letters*, 2013. **39**(1): p.27-29.
- [Kong et al. 2015] L. Kong, Z. Wu, S. Chen, Y. Cao, Y. Zhang, H. Li and J. Kang. "Performance evaluation of multi-junction solar cells by spatially resolved electroluminescence microscopy". *Nanoscale Research Letters*, 2015. **10**(1): p.40.
- [Kroemer 1987] H. Kroemer. "Polar-on-nonpolar epitaxy". *Journal of Crystal Growth*, 1987. **81**(1): p.193-204.
- [Kumar et al. 2010] A. Kumar and C. Zhou. "The Race To Replace Tin-Doped Indium Oxide: Which Material Will Win?". *ACS Nano*, 2010. **4**(1): p.11-14.
- [Kurtz 2009] S. Kurtz. "Opportunities and challenges for development of a mature concentrating photovoltaic power industry". 2009.
- [Kurtz et al. 1992] S. Kurtz, J. Olson, A. Kibbler and K. Bertness. "Incorporation of zinc in MOCVD growth of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ ". *Journal of crystal growth*, 1992. **124**(1-4): p.463-469.
- [Kurtz et al. 1990] S. 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". *Journal of Applied Physics*, 1990. **68**(4): p.1890-1895.
- [Kurtz et al. 1994] S. R. Kurtz, J. Olson, D. Friedman, A. Kibbler and S. Asher. "Ordering and disordering of doped $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ ". *Journal of electronic materials*, 1994. **23**(5): p.431-435.
- [Kuzmenko et al. 2008] A. B. Kuzmenko, E. van Heumen, F. Carbone and D. van der Marel. "Universal Optical Conductance of Graphite". *Physical Review Letters*, 2008. **100**(11): p.117401.
- [Kwon et al. 2012] K. C. Kwon, K. S. Choi and S. Y. Kim. "Increased Work Function in Few-Layer Graphene Sheets via Metal Chloride Doping". *Advanced Functional Materials*, 2012. **22**(22): p.4724-4731.

- [Lange et al. 2011] P. Lange, M. Dorn, N. Severin, D. A. Vanden Bout and J. P. Rabe. "Single- and Double-Layer Graphenes as Ultrabarrriers for Fluorescent Polymer Films". *The Journal of Physical Chemistry C*, 2011. **115**(46): p.23057-23061.
- [Leclercq. J et al. 2016] Leclercq. J and Sveshtarov. P. "The transfer of graphene: a review". *Bulgarian Journal of Physics*, 2016. **43**(2): p.121-147.
- [Lee et al. 2011] C. Lee, J. Y. Kim, S. Bae, K. S. Kim, B. H. Hong and E. J. Choi. "Optical response of large scale single layer graphene". *Applied Physics Letters*, 2011. **98**(7): p.071905.
- [Lee et al. 1993] J. B. Lee, I. Kim, H. K. Kwon and B.-D. Choe. "Amphoteric behavior of germanium in $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ grown by liquid phase epitaxy". *Applied physics letters*, 1993. **62**(14): p.1620-1622.
- [Lee et al. 2001] R. T. Lee, C. M. Fetzer, S. W. Jun, D. C. Chapman, J. K. Shurtleff, G. B. Stringfellow, Y. W. Ok and T. Y. Seong. "Enhancement of compositional modulation in GaInP epilayers by the addition of surfactants during organometallic vapor phase epitaxy growth". *Journal of Crystal Growth*, 2001. **233**(3): p.490-502.
- [Lee et al. 1998] S. H. Lee, C. Fetzer and G. B. Stringfellow. "Effect of Te doping on step structure and ordering in GaInP". *Journal of Crystal Growth*, 1998. **195**(1): p.13-20.
- [Lee et al. 1999] S. H. Lee, C. Y. Fetzer, G. B. Stringfellow, D. H. Lee and T. Y. Seong. "Te doping of GaInP: Ordering and step structure". *Journal of Applied Physics*, 1999. **85**(7): p.3590-3596.
- [LeGoues et al. 1990] F. K. LeGoues, V. P. Kesan, S. S. Iyer, J. Tersoff and R. Tromp. "Surface-stress-induced order in SiGe alloy films". *Physical Review Letters*, 1990. **64**(17): p.2038-2041.
- [Levendorf et al. 2009] M. P. Levendorf, C. S. Ruiz-Vargas, S. Garg and J. Park. "Transfer-Free Batch Fabrication of Single Layer Graphene Transistors". *Nano Letters*, 2009. **9**(12): p.4479-4483.
- [Levesque et al. 2011] P. L. Levesque, S. S. Sabri, C. M. Aguirre, J. Guillemette, M. Siaj, P. Desjardins, T. Szkopek and R. Martel. "Probing Charge Transfer at Surfaces Using Graphene Transistors". *Nano Letters*, 2011. **11**(1): p.132-137.
- [Li et al. 2009] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff. "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils". *Science*, 2009. **324**(5932): p.1312-1314.
- [Li et al. 2015] X. Li, W. Chen, S. Zhang, Z. Wu, P. Wang, Z. Xu, H. Chen, W. Yin, H. Zhong and S. Lin. "18.5% efficient graphene/GaAs van der Waals heterostructure solar cell". *Nano Energy*, 2015. **16**(Supplement C): p.310-319.
- [Li et al. 2010] X. Li, H. Zhu, K. Wang, A. Cao, J. Wei, C. Li, Y. Jia, Z. Li, X. Li and D. Wu. "Graphene-On-Silicon Schottky Junction Solar Cells". *Advanced Materials*, 2010. **22**(25): p.2743-2748.
- [Li et al. 2009] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo and R. S. Ruoff. "Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes". *Nano Letters*, 2009. **9**(12): p.4359-4363.

- [Liang et al. 2011] X. Liang, B. A. Sperling, I. Calizo, G. Cheng, C. A. Hacker, Q. Zhang, Y. Obeng, K. Yan, H. Peng, Q. Li, X. Zhu, H. Yuan, A. R. Hight Walker, Z. Liu, L.-m. Peng and C. A. Richter. "Toward Clean and Crackless Transfer of Graphene". *ACS Nano*, 2011. **5**(11): p.9144-9153.
- [Lin et al. 2016] T.-N. Lin, S. R. M. S. Santiago, J.-A. Zheng, Y.-C. Chao, C.-T. Yuan, J.-L. Shen, C.-H. Wu, C.-A. J. Lin, W.-R. Liu, M.-C. Cheng and W.-C. Chou. "Enhanced Conversion Efficiency of III–V Triple-junction Solar Cells with Graphene Quantum Dots". 2016. **6**: p.39163.
- [Lin et al. 2014] Y.-J. Lin and J.-J. Zeng. "Determination of Schottky barrier heights and Fermi-level unpinning at the graphene/n-type Si interfaces by X-ray photoelectron spectroscopy and Kelvin probe". *Applied Surface Science*, 2014. **322**(Supplement C): p.225-229.
- [Lin et al. 2013] Y. Lin, X. Li, D. Xie, T. Feng, Y. Chen, R. Song, H. Tian, T. Ren, M. Zhong and K. Wang. "Graphene/semiconductor heterojunction solar cells with modulated antireflection and graphene work function". *Energy & Environmental Science*, 2013. **6**(1): p.108-115.
- [Liu et al. 2012] J. Liu, Y. Xue, M. Zhang and L. Dai. "Graphene-based materials for energy applications". *MRS Bulletin*, 2012. **37**(12): p.1265-1272.
- [Liu et al. 2014] W. Liu, S. Kraemer, D. Sarkar, H. Li, P. M. Ajayan and K. Banerjee. "Controllable and Rapid Synthesis of High-Quality and Large-Area Bernal Stacked Bilayer Graphene Using Chemical Vapor Deposition". *Chemistry of Materials*, 2014. **26**(2): p.907-915.
- [Lopes dos Santos et al. 2007] J. M. B. Lopes dos Santos, N. M. R. Peres and A. H. Castro Neto. "Graphene Bilayer with a Twist: Electronic Structure". *Physical Review Letters*, 2007. **99**(25): p.256802.
- [Mak et al. 2010] K. F. Mak, J. Shan and T. F. Heinz. "Electronic Structure of Few-Layer Graphene: Experimental Demonstration of Strong Dependence on Stacking Sequence". *Physical Review Letters*, 2010. **104**(17): p.176404.
- [Massies et al. 1992] J. Massies, N. Grandjean and V. H. Etgens. "Surfactant mediated epitaxial growth of $\text{In}_x\text{Ga}_{1-x}\text{As}$ on GaAs (001)". *Applied Physics Letters*, 1992. **61**(1): p.99-101.
- [Matsuzawa et al. 2000] K. Matsuzawa, K. Uchida and A. Nishiyama. "A unified simulation of Schottky and ohmic contacts". *IEEE Transactions on Electron Devices*, 2000. **47**(1): p.103-108.
- [McClure 1956] J. W. McClure. "Diamagnetism of Graphite". *Physical Review*, 1956. **104**(3): p.666-671.
- [McMahon et al. 2001] W. E. McMahon and J. M. Olson. "A scanning tunneling microscopy study of As/Ge (mnn) and P/Ge (mnn) surfaces". *Journal of crystal growth*, 2001. **225**(2): p.410-414.
- [Munshi et al. 2012] A. M. Munshi, D. L. Dheeraj, V. T. Fauske, D.-C. Kim, A. T. J. van Helvoort, B.-O. Fimland and H. Weman. "Vertically Aligned GaAs Nanowires on Graphite and Few-Layer Graphene: Generic Model and Epitaxial Growth". *Nano Letters*, 2012. **12**(9): p.4570-4576.
- [Muñoz et al. 2013] R. Muñoz and C. Gómez-Aleixandre. "Review of CVD Synthesis of Graphene". *Chemical Vapor Deposition*, 2013. **19**(10-11-12): p.297-322.

- [Na et al. 2006] M. Na and S.-W. Rhee. "Electronic characterization of Al/PMMA[poly(methyl methacrylate)]/p-Si and Al/CEP(cyanoethyl pullulan)/p-Si structures". *Organic Electronics*, 2006. **7**(4): p.205-212.
- [Na et al. 2017] Y. Na, J. Han and J.-S. Yeo. "Approaches to Reduce the Contact Resistance by the Formation of Covalent Contacts in Graphene Thin Film Transistors". *Applied Science and Convergence Technology*, 2017. **26**(4): p.55-61.
- [Nagashio et al. 2010] K. Nagashio, T. Nishimura, K. Kita and A. Toriumi. "Contact resistivity and current flow path at metal/graphene contact". *Applied Physics Letters*, 2010. **97**(14): p.143514.
- [Nair et al. 2008] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres and A. K. Geim. "Fine Structure Constant Defines Visual Transparency of Graphene". *Science*, 2008. **320**(5881): p.1308.
- [Nelson et al. 2010] F. J. Nelson, V. K. Kamineni, T. Zhang, E. S. Comfort, J. U. Lee and A. C. Diebold. "Optical properties of large-area polycrystalline chemical vapor deposited graphene by spectroscopic ellipsometry". *Applied Physics Letters*, 2010. **97**(25): p.253110.
- [Novoselov et al. 2004] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov. "Electric Field Effect in Atomically Thin Carbon Films". *Science*, 2004. **306**(5696): p.666-669.
- [Ochoa-Martinez et al. 2015] E. Ochoa-Martinez, M. Gabas, L. Barrutia, A. Pesquera, A. Centeno, S. Palanco, A. Zurutuza and C. Algora. "Determination of a refractive index and an extinction coefficient of standard production of CVD-graphene". *Nanoscale*, 2015. **7**(4): p.1491-1500.
- [Ochoa et al. 2016] 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)". *Progress in Photovoltaics: Research and Applications*, 2016. **24**(10): p.1332-1345.
- [Oh et al. 2004] J. Oh and J. C. Campbell. "Thermal desorption of Ge native oxides and the loss of Ge from the surface". *Journal of electronic materials*, 2004. **33**(4): p.364-367.
- [Olson et al. 2006] J. M. Olson, M. M, W. E. and S. Kurtz. "Effect of Sb on the Properties of GaInP Top Cells. Book Effect of Sb on the Properties of GaInP Top Cells". *IEEE 4th World Conference on Photovoltaic Energy Conference*, 2006. **1**: p.787-790.
- [Olson et al. 1998] J. M. Olson and W. E. McMahon. "Structure of Ge (100) surfaces for high-efficiency photovoltaic applications". *2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion.*, 1998.
- [Palacios et al. 2010] T. Palacios, A. Hsu and H. Wang. "Applications of graphene devices in RF communications". *IEEE Communications Magazine*, 2010. **48**(6): p.122-128.
- [Paton et al. 2014] K. R. Paton, E. Varrla, C. Backes, R. J. Smith, U. Khan, A. O'Neill, C. Boland, M. Lotya, O. M. Istrate, P. King, T. Higgins, S. Barwich, P. May, P. Puczkarski, I. Ahmed, M. Moebius, H. Pettersson, E. Long, J. Coelho, S. E. O'Brien, E. K. McGuire, B. M. Sanchez, G. S. Duesberg, N. McEvoy, T. J. Pennycook, C. Downing, A. Crossley, V. Nicolosi and J. N. Coleman. "Scalable production of large quantities of defect-free few-layer graphene by shear exfoliation in liquids". *Nat Mater*, 2014. **13**(6): p.624-630.

- [Pi et al. 2009] K. Pi, K. M. McCreary, W. Bao, W. Han, Y. F. Chiang, Y. Li, S. W. Tsai, C. N. Lau and R. K. Kawakami. "Electronic doping and scattering by transition metals on graphene". *Physical Review B*, 2009. **80**(7): p.075406.
- [Pirkle et al. 2011] A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel, R. S. Ruoff and R. M. Wallace. "The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO₂". *Applied Physics Letters*, 2011. **99**(12): p.122108.
- [Ponomarenko et al. 2009] L. A. Ponomarenko, R. Yang, T. M. Mohiuddin, M. I. Katsnelson, K. S. Novoselov, S. V. Morozov, A. A. Zhukov, F. Schedin, E. W. Hill and A. K. Geim. "Effect of a High- κ Environment on Charge Carrier Mobility in Graphene". *Physical Review Letters*, 2009. **102**(20): p.206603.
- [Rao et al. 2010] C. N. R. Rao, A. K. Sood, R. Voggu and K. S. Subrahmanyam. "Some Novel Attributes of Graphene". *The Journal of Physical Chemistry Letters*, 2010. **1**(2): p.572-580.
- [Reina et al. 2009] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus and J. Kong. "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition". *Nano Letters*, 2009. **9**(1): p.30-35.
- [Robinson et al. 2011] J. A. Robinson, M. LaBella, M. Zhu, M. Hollander, R. Kasarda, Z. Hughes, K. Trumbull, R. Cavaleiro and D. Snyder. "Contacting graphene". *Applied Physics Letters*, 2011. **98**(5): p.053103.
- [Ryu et al. 2010] S. Ryu, L. Liu, S. Berciaud, Y.-J. Yu, H. Liu, P. Kim, G. W. Flynn and L. E. Brus. "Atmospheric Oxygen Binding and Hole Doping in Deformed Graphene on a SiO₂ Substrate". *Nano Letters*, 2010. **10**(12): p.4944-4951.
- [Sabnis et al. 2012] V. Sabnis, H. Yuen and M. Wiemer. "High-efficiency multijunction solar cells employing dilute nitrides". *AIP Conference Proceedings*, 2012. **1477**(1): p.14-19.
- [Sasaki et al. 2013] K. Sasaki, T. Agui, K. Nakaido, N. Takahashi, R. Onitsuka and T. Takamoto. "Development of InGaP/GaAs/InGaAs inverted triple junction concentrator solar cells". *AIP Conference Proceedings*, 2013. **1556**(1): p.22-25.
- [Schedin et al. 2007] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson and K. S. Novoselov. "Detection of individual gas molecules adsorbed on graphene". *Nat Mater*, 2007. **6**(9): p.652-655.
- [Schulte et al. 2013] K. L. Schulte, A. W. Wood, R. C. Reedy, A. J. Ptak, N. T. Meyer, S. E. Babcock and T. F. Kuech. "Heteroepitaxy of GaAs on (001) $\Rightarrow$ 6° Ge substrates at high growth rates by hydride vapor phase epitaxy". *Journal of Applied Physics*, 2013. **113**(17): p.174903.
- [Semenoff 1984] G. W. Semenoff. "Condensed-Matter Simulation of a Three-Dimensional Anomaly". *Physical Review Letters*, 1984. **53**(26): p.2449-2452.
- [Shi et al. 2014] X. Shi, G. Dong, M. Fang, F. Wang, H. Lin, W.-C. Yen, K. S. Chan, Y.-L. Chueh and J. C. Ho. "Selective n-type doping in graphene via the aluminium nanoparticle decoration approach". *Journal of Materials Chemistry C*, 2014. **2**(27): p.5417-5421.
- [Shi et al. 2010] Y. Shi, K. K. Kim, A. Reina, M. Hofmann, L.-J. Li and J. Kong. "Work Function Engineering of Graphene Electrode via Chemical Doping". *ACS Nano*, 2010. **4**(5): p.2689-2694.

- [Shurtleff et al. 1999] J. K. Shurtleff, R. T. Lee, C. M. Fetzer and G. B. Stringfellow. "Band-gap control of GaInP using Sb as a surfactant". *Applied Physics Letters*, 1999. **75**(13): p.1914-1916.
- [Singh et al. 2013] A. K. Singh, M. Ahmad, V. K. Singh, K. Shin, Y. Seo and J. Eom. "Tailoring the Electrical Properties of Graphene Layers by Molecular Doping". *ACS Applied Materials & Interfaces*, 2013. **5**(11): p.5276-5281.
- [Singh et al. 2012] A. K. Singh, M. W. Iqbal, V. K. Singh, M. Z. Iqbal, J. H. Lee, S.-H. Chun, K. Shin and J. Eom. "Molecular n-doping of chemical vapor deposition grown graphene". *Journal of Materials Chemistry*, 2012. **22**(30): p.15168-15174.
- [Software.D.S 2015] Software.D.S. "Atlas User ' s Manual ". 2015(no 408): p.567–1000.
- [Somani et al. 2006] P. R. Somani, S. P. Somani and M. Umeno. "Planer nano-graphenes from camphor by CVD". *Chemical Physics Letters*, 2006. **430**(1): p.56-59.
- [Sonde et al. 2009] S. Sonde, F. Giannazzo, V. Raineri, R. Yakimova, J. R. Huntzinger, A. Tiberj and J. Camassel. "Electrical properties of the graphene/4H-SiC (0001) interface probed by scanning current spectroscopy". *Physical Review B*, 2009. **80**(24): p.241406.
- [Stan et al. 2008] M. A. Stan, N. Y. Li, F. A. Spadafora, H. Q. Hou, P. R. Sharps and N. S. Fatemi 2008, Apparatus and method for optimizing the efficiency of germanium junctions in multi-junction solar cells. US7339109 B2.
- [Stringfellow et al. 2000] G. B. Stringfellow, R. T. Lee, C. M. Fetzer, J. K. Shurtleff, Y. Hsu, S. W. Jun, S. Lee and T. Y. Seong. "Surfactant effects of dopants on ordering in GaInP". *Journal of Electronic Materials*, 2000. **29**(1): p.134-139.
- [Su et al. 2011] C.-Y. Su, A.-Y. Lu, C.-Y. Wu, Y.-T. Li, K.-K. Liu, W. Zhang, S.-Y. Lin, Z.-Y. Juang, Y.-L. Zhong, F.-R. Chen and L.-J. Li. "Direct Formation of Wafer Scale Graphene Thin Layers on Insulating Substrates by Chemical Vapor Deposition". *Nano Letters*, 2011. **11**(9): p.3612-3616.
- [Su et al. 1994] L. C. Su, I. H. Ho and G. B. Stringfellow. "Control of ordering in Ga_{0.5}In_{0.5}P using growth temperature". *Journal of Applied Physics*, 1994. **76**(6): p.3520-3525.
- [Suk et al. 2011] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg and R. S. Ruoff. "Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates". *ACS Nano*, 2011. **5**(9): p.6916-6924.
- [Suk et al. 2013] J. W. Suk, W. H. Lee, J. Lee, H. Chou, R. D. Piner, Y. Hao, D. Akinwande and R. S. Ruoff. "Enhancement of the Electrical Properties of Graphene Grown by Chemical Vapor Deposition via Controlling the Effects of Polymer Residue". *Nano Letters*, 2013. **13**(4): p.1462-1467.
- [Sun et al. 2016] Y. Sun, X. Zhang, L. Wang, L. Zhang, S. Raju and M. Chan 2016. Interlayer Conductance of Graphene with Multiple Transfer Process.
- [Takahashi et al. 1985] T. Takahashi, H. Tokailin and T. Sagawa. "Angle-resolved ultraviolet photoelectron spectroscopy of the unoccupied band structure of graphite". *Physical Review B*, 1985. **32**(12): p.8317-8324.

- [Taylor et al. 2015] M. Taylor, P. Ralon and A. Ilaş. "The power to change: solar and wind cost reduction potential to 2025. ". *International Renewable Energy Agency (IRENA)*, 2015.
- [Tobías et al. 2002] I. Tobías and A. Luque. "Ideal efficiency of monolithic, series-connected multijunction solar cells". *Progress in Photovoltaics: Research and Applications*, 2002. **10**(5): p.323-329.
- [Tobin et al. 1988] S. P. Tobin, S. Vernon, C. Bajgar, V. Haven, L. Geoffroy and D. Lillington. "High-efficiency GaAs/Ge monolithic tandem solar cells". *IEEE electron device letters*, 1988. **9**(5): p.256-258.
- [Tongay et al. 2012] S. Tongay, M. Lemaitre, X. Miao, B. Gila, B. R. Appleton and A. F. Hebard. "Rectification at Graphene-Semiconductor Interfaces: Zero-Gap Semiconductor-Based Diodes". *Physical Review X*, 2012. **2**(1): p.011002.
- [Tongay et al. 2009] S. Tongay, T. Schumann and A. F. Hebard. "Graphite based Schottky diodes formed on Si, GaAs, and 4H-SiC substrates". *Applied Physics Letters*, 2009. **95**(22): p.222103.
- [Tsao et al. 2006] J. Tsao, N. Lewis and G. Crabtree. "Solar FAQs". *US department of Energy*, 2006.
- [van Riesen et al. 2015] S. van Riesen, M. Neubauer, A. Boos, M. M. Rico, C. Gourdel, S. Wanka, R. Krause, P. Guernard, A. Gombert and G. Siefert. "New module design with 4-junction solar cells for high efficiencies". AIP Conference Proceedings, 2015: AIP Publishing.
- [Wallace 1947] P. R. Wallace. "The Band Theory of Graphite". *Physical Review*, 1947. **71**(9): p.622-634.
- [Wan et al. 2011] X. Wan, G. Long, L. Huang and Y. Chen. "Graphene – A Promising Material for Organic Photovoltaic Cells". *Advanced Materials*, 2011. **23**(45): p.5342-5358.
- [Wang et al. 2013] G. Wang, M. Zhang, Y. Zhu, G. Ding, D. Jiang, Q. Guo, S. Liu, X. Xie, P. K. Chu, Z. Di and X. Wang. "Direct Growth of Graphene Film on Germanium Substrate". 2013. **3**: p.2465.
- [Wang et al. 2009] H. Wang, X. Wang, X. Li and H. Dai. "Chemical self-assembly of graphene sheets". *Nano Research*, 2009. **2**(4): p.336-342.
- [Wang et al. 2009] X. Wang, X. Li, L. Zhang, Y. Yoon, P. K. Weber, H. Wang, J. Guo and H. Dai. "N-Doping of Graphene Through Electrothermal Reactions with Ammonia". *Science*, 2009. **324**(5928): p.768-771.
- [Wang et al. 2015] X. Wang and F. Xia. "Van der Waals heterostructures: Stacked 2D materials shed light". *Nat Mater*, 2015. **14**(3): p.264-265.
- [Wang et al. 2011] Y. Wang, Y. Zheng, X. Xu, E. Dubuisson, Q. Bao, J. Lu and K. P. Loh. "Electrochemical Delamination of CVD-Grown Graphene Film: Toward the Recyclable Use of Copper Catalyst". *ACS Nano*, 2011. **5**(12): p.9927-9933.
- [Wang. H et al. 2012] Wang. H, A. Hsu and T. Palacios. "Graphene Electronics for RF Applications". *IEEE Microwave Magazine*, 2012. **13**(4): p.114-125.

- [Wanlass 1990] M. W. Wanlass 1990, Method of passivating semiconductor surfaces. Google Patents.
- [Watanabe et al. 2012] E. Watanabe, A. Conwill, D. Tsuya and Y. Koide. "Low contact resistance metals for graphene based devices". *Diamond and Related Materials*, 2012. **24**(Supplement C): p.171-174.
- [Welser et al. 2008] E. Welser, W. Guter, A. Wekkeli and F. Dimroth. "Memory effect of Ge in III–V semiconductors". *Journal of Crystal Growth*, 2008. **310**(23): p.4799-4802.
- [Wiesenfarth et al. 2017] M. Wiesenfarth, S. P. Philipps, A. W. Bett, K. Horowitz and S. Kurtz 2017, Current Status of Concentrator Photovoltaic (CPV) Technology, version 1.3. NREL (National Renewable Energy Laboratory (NREL), Golden, CO (United States).
- [Withers et al. 2015] F. Withers, O. Del Pozo-Zamudio, A. Mishchenko, A. P. Rooney, A. Gholinia, K. Watanabe, T. Taniguchi, S. J. Haigh, A. K. Geim, A. I. Tartakovskii and K. S. Novoselov. "Light-emitting diodes by band-structure engineering in van der Waals heterostructures". *Nat Mater*, 2015. **14**(3): p.301-306.
- [Wu et al. 2016] H.-M. Wu, S.-J. Tsai, H.-I. Ho and H.-H. Lin. "Ge auto-doping and out-diffusion in InGaP grown on Ge substrate and their effects on the ordering of InGaP". *Journal of Applied Physics*, 2016. **119**(11): p.115302.
- [Wu et al. 2014] M. Wu, E. Luna, J. Puustinen, M. Guina and A. Trampert. "Observation of atomic ordering of triple-period-A and -B type in GaAsBi". *Applied Physics Letters*, 2014. **105**(4): p.041602.
- [Yan et al. 2011] K. Yan, H. Peng, Y. Zhou, H. Li and Z. Liu. "Formation of Bilayer Bernal Graphene: Layer-by-Layer Epitaxy via Chemical Vapor Deposition". *Nano Letters*, 2011. **11**(3): p.1106-1110.
- [Yang et al. 2011] C. Yang, S. Lee, K. Wook Shin, S. Oh, J. Park, C.-Z. Kim, W.-K. Park, S.-K. Ha, W. Jun Choi and E. Yoon. "Growth of Si-doped GaInP on Ge-on-Si substrates and its photoluminescence characteristics". *Applied Physics Letters*, 2011. **99**(9): p.091904.
- [Yang et al. 2009] L. Yang, J. Deslippe, C.-H. Park, M. L. Cohen and S. G. Louie. "Excitonic Effects on the Optical Response of Graphene and Bilayer Graphene". *Physical Review Letters*, 2009. **103**(18): p.186802.
- [Yang et al. 2010] N. Yang, J. Zhai, D. Wang, Y. Chen and L. Jiang. "Two-Dimensional Graphene Bridges Enhanced Photoinduced Charge Transport in Dye-Sensitized Solar Cells". *ACS Nano*, 2010. **4**(2): p.887-894.
- [Yi et al. 2011] Y. Yi, W. M. Choi, Y. H. Kim, J. W. Kim and S. J. Kang. "Effective work function lowering of multilayer graphene films by subnanometer thick AlO_x overlayers". *Applied Physics Letters*, 2011. **98**(1): p.013505.
- [Yong-Jin et al. 2012] K. Yong-Jin, K. Sang Jin, J. Myung Hee, C. Kwang Yeol, B. Sukang, L. Seoung-Ki, L. Youngbin, S. Dolly, L. Bora, S. Huiyoun, C. Myungshin, P. Kyuho, A. Jong-Hyun and H. Byung Hee. "Low-temperature growth and direct transfer of graphene-graphitic carbon films on flexible plastic substrates". *Nanotechnology*, 2012. **23**(34): p.344016.

[Yoon et al. 2001] I. Yoon, S. Han, H. Park and T. Kim. "Amphoteric behavior of Ge dopants in $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ epilayers grown on GaAs (100) substrates". *Journal of Physics and Chemistry of Solids*, 2001. **62**(3): p.607-611.

[Yu et al. 2011] Q. Yu, L. A. Jauregui, W. Wu, R. Colby, J. Tian, Z. Su, H. Cao, Z. Liu, D. Pandey, D. Wei, T. F. Chung, P. Peng, N. P. Guisinger, E. A. Stach, J. Bao, S.-S. Pei and Y. P. Chen. "Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition". *Nat Mater*, 2011. **10**(6): p.443-449.

[Yu et al. 2009] Y.-J. Yu, Y. Zhao, S. Ryu, L. E. Brus, K. S. Kim and P. Kim. "Tuning the Graphene Work Function by Electric Field Effect". *Nano Letters*, 2009. **9**(10): p.3430-3434.

[Zaretski et al. 2015] A. V. Zaretski and D. J. Lipomi. "Processes for non-destructive transfer of graphene: widening the bottleneck for industrial scale production". *Nanoscale*, 2015. **7**(22): p.9963-9969.

[Zhang et al. 2009] Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen and F. Wang. "Direct observation of a widely tunable bandgap in bilayer graphene". *Nature*, 2009. **459**(7248): p.820-823.

[Zhu et al. 2014] S.-E. Zhu, S. Yuan and G. C. A. M. Janssen. "Optical transmittance of multilayer graphene". *EPL (Europhysics Letters)*, 2014. **108**(1): p.17007.

[Zhu et al. 2014] Z. Zhu, J. Ma, Z. Wang, C. Mu, Z. Fan, L. Du, Y. Bai, L. Fan, H. Yan, D. L. Phillips and S. Yang. "Efficiency Enhancement of Perovskite Solar Cells through Fast Electron Extraction: The Role of Graphene Quantum Dots". *Journal of the American Chemical Society*, 2014. **136**(10): p.3760-3763.

Journal Publications

- [1]. P.Espinet-Gonzalez, E.Barrigón, E.García-Tabarés, M.Ochoa, **L.Barrutia**, V.Orlando, P.Huo, J.Bautista, I.García, N.Nuñez, M.Vazquez, I.Rey-Stolle y C.Algora. “Concentración Fotovoltaica”. Revista Española de Física v. 27 (n. 2); pp. 35-37. ISSN 0213-862X (2013).
- [2]. **L.Barrutia**, E.Barrigón, I.García, I.Rey-Stolle and .C.Algora. “Highly conductive p++-AlGaAs/n++-GaInP tunnel junctions for operation up to 15,000 suns in concentrator solar cells”. Semiconductor today: Compounds & Advanced Silicon. pp. 80-81. ISSN 1752-2935 (2014).
- [3]. E. Barrigón, I.García, **L. Barrutia**, I.Rey-Stolle, and C.Algora. “Highly Conductive p++-AlGaAs/n++-GaInP Tunnel Junction for Ultra-High Concentrator Solar Cells”. Progress in Photovoltaics, 22, (2014) pp.399-404.
- [4]. E.Ochoa-Martinez, M.Gabás, **L.Barrutia**, A.Pesquera, A. Centeno, S.Palanco, A.Zurutuza, C Algora. “Determination of refractive index and extinction coefficient of standard production CVD-graphene” Nanoscale (2015). DOI: 10.1039/C4NR06119E.
- [5]. E. Barrigón, **L.Barrutia**, I. Rey-Stolle. “Optical in situ calibration of Sb for growing disordered GaInP by MOVPE”. Journal of Crystal Growth 426, (2015) pp 71-74.
- [6]. E. Barrigón, **L.Barrutia**, M.Ochoa, I. Rey-Stolle, C.Algora. “Effect of Sb on the Quantum efficiency of GaInP Solar Cells”. Progress in Photovoltaics, Vol 24, n8, (2015) pp 1116-1122.
- [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 (1,000-5,000 suns)". Progress in Photovoltaics, Vol 24, n10 (2015), pp 1332-1345.

- [8]. C.Coll, E.Barrigón, L.López-Conesa, J.Rebled, **L.Barrutia**, I.Rey-Stolle, S.Estradé, C.Algora and F.Peiró. “The effect of Sb-surfactant on GaInP CuP B type ordering: assessment through dark field TEM and aberration corrected – HAADF”. *Physical Chemistry Chemical Physics* (2017) DOI: 10.1039/C7CP01125C.
- [9]. **L.Barrutia**, E.Barrigón, I.García, I.Rey-Stolle and C.Algora. “Effect of Ge autodoping during III-V MOVPE growth on Ge substrates” *Journal of Crystal Growth* (2017). DOI: 10.1016/j.jcrysgro.2017.06.022.
- [10].E.Barrigón, M.Ochoa, I.García, **L.Barrutia**, I. Rey-Stolle, C.Algora "Degradation of Ge subcells by thermal load during the growth of multijunction solar cells" *Progress in Photovoltaics*. (2017). DOI: 10.1002/pip.2948.
- [11].E.Ochoa-Martinez, **L.Barrutia**, M.Ochoa, E.Barrigón, I.García, I.Rey-Stolle, C.Algora, P.Basa, G.kronome and M.Gabas. “Refractive indexes and extinction coefficients of n- and p- type doped GaInP and AlGaInP for multijunction solar cells”. *Solar Energy Materials and Solar Cells*, (2018).174 p:388-396.

Contributions to national and international conferences

- [1]. P.Espinet-Gonzalez, E.Barrigón, M.Ochoa, **L.Barrutia**, V.Orlando, C.Algora, and I.Rey-Stolle. “Structural challenges in multijunction solar cells for ultrahigh CPV”. Oral presentation at 27th European Photovoltaic Solar Energy Conference (EU PVSEC) and Exhibition. Frankfurt, Germany, (September 2012).

- [2]. P. Espinet-González, C. Algora, V. Orlando, N. Nuñez, M. Vázquez, J. Bautista, H. Xiugang, **L. Barrutia**, I. Rey-Stolle and K. Araki. “Preliminary temperature accelerated life test (ALT) on III-V commercial concentrator triple junction solar cells”. Oral presentation at 38th IEEE Photovoltaic Specialists. Austin, Texas, USA (2012).

- [3]. E.Barrigón, P. Espinet-González, Y. Contreras, **L.Barrutia**, I.Rey-Stolle, C. Algora. “On the Use of I-V Curves as a Diagnosis Tool for Proper External Quantum Efficiency Measurements of Multijunction Solar Cells”. Oral presentation at 40th IEEE Photovoltaics Specialist Conference, Denver, Colorado, USA (June 2014).

- [4]. E. Ochoa-Martínez, M. Gabás, **L. Barrutia**, M. Ochoa, Carlos Algora. “Influence of Doping on the Optical Response of GaInP”. Oral presentation at 10th Spanish Conference on Electron Devices. Aranjuez, Spain (February 2015).

- [5]. C. Algora, I. Rey-Stolle, E. Barrigón, I. García, M. Vázquez, N. Núñez, R. Peña. P. Espinet, M. Ochoa, L. Ayllón, **L. Barrutia**, V. Orlando, H. Pengyun, M. Gabás and S. Palanco, C. Ballesteros and B. Galiana. “New Generation Architectures in III-V Multijunction Solar Cells for Efficiencies of 50%”. Oral presentation at 10th Spanish Conference on Electron Devices. Aranjuez, Spain (February 2015).

- [6]. C. Coll, Ll. López, E. Barrigón, **L.Barrutia**, I. Rey-Stolle, S. Estradé, F.Peiró. “Degree of ordering as a function of Sb content in $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ layers for tandem solar cells”. Oral presentation at 10th Spanish Conference on Electron Devices. Aranjuez, Spain (February 2015).

- [7]. M.Ochoa, E.Barrigón, **L.Barrutia**, I.Rey-Stolle and C.Algora. “Key aspects on semiconductor structure design for ultra-high concentration multi-junction solar cells”. Oral presentation at 11th International Conference on Concentrator Photovoltaic Systems. Aix-les-Bains, France (April 2015).

- [8]. **L. Barrutia**, E. Barrigón, LL. López-Conesa, J.Rebled, S. Estradé, F. Peiró, I. Rey-Stolle, C. Algora. “On the use of Sb to improve the Performance of GaInP subcells of Multijunction Solar Cells”. Poster Presentation at 42th IEEE Photovoltaics Specialist Conference, Nueva Orleans, USA (June 2015).

- [9]. **L.Barrutia**, E.Barrigón, I. Rey-Stolle and C.Algora. “Effect of Ge autodoping during III-V on Ge epitaxy by MOVPE”. Oral presentation at 18th International Conference Metal Organic Phase Epitaxy. San Diego, California, USA (July 2016).

- [10]. I.Rey-Stolle, I.García, E.Barrigón, J.Olea, D.Pastor, M.Ochoa, **L.Barrutia**, C.Algora. “On the Thermal Degradation of Tunnel Diodes in Multijunction Solar Cells”. Oral presentation at 13th International Conference on Concentration Photovoltaic Systems. Ottawa, Canda (May 2017).

Patents

- [1]. 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).