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Tesis doctoral

Structures based on GaAs(Sb)(N) semiconductor alloys for high efficiency multi-junction solar cells

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El tribunal nombrado por el Mgfco. Y Excmo. Sr. Rector de la Universidad Politécnica de Madrid, el día de de 2019, para juzgar la Tesis arriba indicada, compuesto por los siguientes doctores:

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**A mi familia y todos mis seres queridos,
gracias por acompañarme.**

“— ¿Doctor en qué?
— Quiere decir doctor en Eruditología”
(*El mago de Oz*)

Abstract

III-V multi-junction solar cells (MJSCs) have hold record conversion efficiencies for many years, which is currently approaching 50 %. Theoretical efficiency limits are calculated using optimum designs with the right lattice constant-bandgap energy combination, which requires a 1.0–1.15 eV bandgap semiconductor material lattice-matched to GaAs/Ge. Insertion of such a material layer in a 4-junction MJSC could lead to an efficiency of 60 % under solar concentration, which would represent a significant breakthrough in photovoltaics. Therefore, 1.0–1.15 eV bandgap materials that can be grown lattice-matched to GaAs/Ge are being nowadays intensively researched.

Dilute nitrides, such as $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ or $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$, are the most suitable candidates: the introduction of a small amount of N in the GaAs matrix sharply reduces the bandgap energy, and at the same time the lattice constant can be adjusted to that of GaAs/Ge. In particular, $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ has many potential advantages over $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$, such as promoting a more efficient N incorporation and reducing the formation of N-related defects. However, quaternary dilute nitrides, even $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$, unavoidably suffer from inherent material problems that seriously degrade carrier dynamics, which are likely the reason for the lack of success of the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ based solar cells up to now.

In this Thesis, we demonstrate that the substitution of the conventional quaternary alloy by a strain-balanced $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ superlattice (SL) with a type-II band alignment is a suitable approach to form the lattice-matched 1.0–1.15 eV subcell to be implemented in the optimum monolithic multi-junction solar cell design. The spatial separation of Sb and N atoms avoids the ubiquitous growth problems, providing an accurate composition control and improving the crystal quality. Moreover, these new structures allow for additional control of the effective bandgap through the period thickness. The type-II band alignment provides long carrier lifetimes, which are also tunable down to the values of the bulk alloys by reducing the period thickness. A reduced period thickness in type-II SLs also results in enhanced absorption due to increased wavefunction overlap, as well as in a change in the transport regime from diffusive to quasi-ballistic, which provides improved carrier extraction efficiency.

For the “low” N and Sb contents required in the ~ 1.15 eV structures, single-junction SL solar cells do not overcome the equivalent bulk devices (the latter having double amount of N and Sb) in terms of power conversion efficiency (*PCE*). Nevertheless, for the higher N and Sb contents required in the ~ 1.0 eV structures, the SL approach is advantageous in terms of solar cell *PCE*. Indeed, 3 nm period SL solar cells show an enhanced *PCE* of 134 % over the equivalent bulk devices. The improvement is attributed to a reduced non-radiative recombination and an improved composition homogeneity in the SLs.

To fully exploit the potential of type-II SLs in photovoltaics, an adequate rapid thermal annealing (RTA) cycle might be applied to the structures. The RTA is shown to reduce the density of N-induced sub-bandgap radiative states, which seems to be the main reason for the enhancement of the open-circuit voltage (V_{OC}) observed after RTA, particularly in the “low” N content ~ 1.15 eV structures. The results suggest that radiative recombination in a broad band of deep defect states is a source of V_{OC} degradation in as-grown GaAs(Sb)(N)-based solar cells. In solar cells with higher N and Sb contents and ~ 1.0 eV bandgap, not only V_{OC} but also short-circuit current density (J_{SC}) is strongly increased after RTA, resulting in substantial enhancements of the *PCE*. The large increase of J_{SC} after RTA in ~ 1.0 eV samples is particularly relevant since it could help to provide current matching when integrated in a MJSC.

Resumen

Las células solares de multi-unión basadas en aleaciones semiconductoras III-V han ostentado el récord de eficiencia de conversión energética durante muchos años, que actualmente se aproxima al 50 %. Cálculos teóricos de eficiencia límite, para los que se emplean diseños optimizados con la correcta combinación de parámetros de red y de energía de bandgap, determinan que es necesario obtener un material semiconductor de 1,0–1,15 eV ajustado en red al GaAs o el Ge. El uso de dicho material para formar una de las capas de una célula de 4 uniones podría permitir alcanzar una eficiencia del 60 % bajo concentración solar, lo que supondría un gran hito en el campo de la energía fotovoltaica. Por lo tanto, actualmente se están realizando grandes esfuerzos para investigar materiales con bandgap de 1,0–1,15 eV que puedan crecerse ajustados a la red del GaAs o del Ge.

Los nitruros diluidos, como son el $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ o el $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$, son candidatos prometedores: en ellos, la introducción de un pequeño porcentaje de N conlleva una fuerte reducción de la energía de bandgap, mientras que su constante de red puede ajustarse a la del GaAs o el Ge. Específicamente el $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ presenta ciertas ventajas frente al $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$, como son una incorporación más eficiente del N y una menor formación de defectos relacionados con la presencia del N. Sin embargo, los nitruros diluidos, incluyendo el $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$, se enfrentan a problemas inherentes a su crecimiento cuaternario que degradan seriamente la dinámica de sus portadores, lo que probablemente sea el motivo de la falta de éxito de las células solares basadas en $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ que se ha observado hasta el momento.

En esta tesis se demuestra que la sustitución de la aleación cuaternaria por una superred de $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ con alineamiento tipo-II puede ser útil para obtener la capa de 1,0–1,15 eV ajustada en red que se desea implementar en la célula monolítica de multi-unión previamente diseñada. Por un lado, la separación espacial de los átomos de N y Sb evita los problemas de crecimiento del cuaternario, y además este tipo de estructura permite un control extra de la energía efectiva del bandgap a través del grosor de su periodo. Por otro lado, el alineamiento de tipo-II proporciona mayores tiempos de vida radiativos, que pueden llegar a reducirse a los tiempos propios del material cuaternario reduciendo el grosor de periodo. Además, la reducción del grosor de periodo en las superredes tipo-II conlleva mejoras en la absorción debido al solapamiento de las funciones de onda, así como

el cambio en el régimen de transporte de portadores de difusivo a cuasi-balístico, lo que mejora la eficiencia de extracción de cargas.

En estructuras con bajos contenidos de N y Sb (aquellos requeridos para obtener estructuras con energía de bandgap de $\sim 1,15$ eV) el desempeño como célula solar de una única unión de las superredes $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ no supera al de células de capas gruesas de $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ equivalentes (las cuales contienen el doble de N y Sb) en términos de eficiencia de conversión. Sin embargo, para contenidos de N y Sb mayores (aquellos requeridos para obtener estructuras con energía de bandgap de $\sim 1,0$ eV), las células solares de superred son claramente superiores a las células gruesas en términos de eficiencia de conversión. De hecho, superredes con un grosor de período de 3 nm muestran una mejora en eficiencia del 134 % comparadas con células gruesas equivalentes. La mejora se atribuye a la disminución de la recombinación no-radiativa y a la mayor homogeneidad en la composición de las superredes.

Para explotar plenamente las ventajas fotovoltaicas de las superredes tipo-II, se ha aplicado un proceso de recocido térmico rápido a las diferentes estructuras. El recocido térmico reduce la densidad de estados de defectos radiativos inducidos por la presencia de N, lo que parece ser la causa de la mejora en el voltaje de circuito abierto (V_{OC}) observada después del recocido, especialmente en las células solares de bajo contenido de N con bandgap de $\sim 1,15$ eV. Los resultados sugieren que la recombinación radiativa que proviene de estados de defectos de N es fuente de degradación para el V_{OC} en las células solares basadas en $\text{GaAs}(\text{Sb})(\text{N})$ sin recocer. En células solares con altos contenidos de N y Sb con bandgap de $\sim 1,0$ eV, no solo el V_{OC} sino también la densidad de corriente de circuito abierto (J_{SC}) se incrementa notablemente después del proceso de recocido, lo que conlleva una gran mejora en la eficiencia de conversión de dichas células. El gran incremento de J_{SC} después del recocido térmico en células solares con energía de bandgap de $\sim 1,0$ eV es de especial interés, ya que podría mejorar el ajuste de corrientes entre sub-células al integrar estas estructuras en células solares de multi-unión.

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List of abbreviations

ADF	Annular Dark Field
AM	Air Mass
ARC	Anti-reflection Coating
BAC	Band Anti-Crossing
BEP	Beam Equivalent Pressure
BF	Bright Field
BSF	Back Surface Field
CB	Conduction band
CCE	Carrier Collection Efficiency
CV	Capacitance-Voltage
DBAC	Double Band Anti-Crossing
DF	Dark Field
DLTS	Deep Level-Transit Spectroscopy
EDX	Energy Dispersive X-ray
EELS	Electron Energy Loss Spectroscopy
EQE	External Quantum Efficiency
FF	Fill Factor
FWHM	Full Width at Half Maximum
FZ	Float zone
HAADF	High Angle Annular Dark Field
IB	Intermediate band
IBSC	Intermediate band solar cell
ICP	Inductively induced plasma
II	Integrated Intensity
IMM	Inverted-Metamorphic
I_{sc}	Short-circuit current
IV	Current voltage
J_{sc}	Short-circuit current density
JV	Current density voltage
LAADF	Low Angle Annular Dark Field
MBE	Molecular Beam Epitaxy
MFC	Mass Flow Controller
MJSC	Multi-junction solar cell

ML	Monolayer
MM	Metamorphic
MOVPE	Metalorganic Vapor Phase Epitaxy
MQW	Multi-quantum well
NEGF	Non-equilibrium Green's function
OED	Optical Emission Detection
P/A	Perimeter/area ratio
PBN	Pyrolytic Boron Nitride
PC	Photocurrent
PCE	Power Conversion Efficiency
PL	Photoluminescence
P_M	Maximum Power
PR	Photoreflectance
PV	Photovoltaics
QD	Quantum dot
QTH	Quartz-tungsten-halogen
QW	Quantum well
RF	Radio frequency
RHEED	Reflective High-Energy Electron Diffraction
R_S	Series resistance
R_{SH}	Shunt resistance
RTA	Rapid Thermal Annealing
SAD	Statistical atomic displacement
SL	Superlattice
SQ limit	Shockley-Queisser efficiency limit
SRH	Shockley-Read-Hall
STEM	Scanning Transmission Electron Microscopy
TDF	Third derivative functional form
TEM	Transmission Electron Microscopy
TR-PL	Time-resolved Photoluminescence
UHV	Ultra-high vacuum
VB	Valence band
V_{oc}	Open-circuit voltage
W_{oc}	Bandgap-voltage offset under open-circuit conditions
XRD	X-ray Diffraction
X-STM	Cross-Sectional Scanning Tunneling Microscopy

1. Introduction and objectives

1.1. Global energy consumption and energetic transition

For the last fifty years, the world has seen a rapidly increasing demand for energy, and there is consensus that this rising trend will continue. In 2016, the World Energy Council produced a set of different plausible scenarios in which the final energy consumption is projected to increase from 22 % to 46 % by 2060 [1].

Burning of fossil fuels (coal, oil and natural gas) has been, and it is still the primary source to satisfy energy demands: in 2014, it constituted 81 % of the total energy consumption [1]. Fossil fuel combustion results in CO₂ and other greenhouse gasses emissions, which cause the burdensome phenomenon known as global warming, consisting in a long-term rise in the average Earth temperature.

The Paris climate agreement, reached by nearly 200 countries in 2015, pursues to hold the average global temperature rise well below 2 °C in the present century, compared to pre-industrial levels. However, if the current CO₂ emission trend is not mitigated, the limit of 2 °C increment will be reached by 2037 [2]. Therefore, from now on the global energy system must undergo a profound and comprehensive transformation that requires a concerted worldwide effort. Shift electricity production from fossil fuels to clean and renewable energy sources along with research in more efficient energy generation hold the key for a technically and economically feasible global energy solution.

In the field of renewable energies, solar energy will be decisive in the energetic transition. Unlike fossil fuels, solar energy is a limitless resource: the solar energy that reaches the Earth's surface in one hour is estimated to be roughly equal to the total energy used globally in a year [3]. Solar energy production has been steadily growing during the last decade, and the increase is likely to continue at an unprecedented rate, meanwhile cost per watt has been gradually falling off. As it is shown in Figure 1.1, a 1 % of electricity was obtained from solar photovoltaics (PV) in 2015, but it will account for 22 % of power generation by 2050 [2]. Continued technical innovations suggest that solar PV costs will go down further in the future. Meanwhile, significant advances have been made to increase the solar energy conversion efficiency; both factors are crucial for the development of PV

technology, which is close to reach the point when it would be technically feasible that PV replaces a significant fraction of the actual electricity generation infrastructure.

Figure 1.1: Rising importance of renewable energies in the power sector (taken from ref. [2]).

1.2. Seeking for high efficiency in solar cells

The conversion efficiency of a solar cell is defined as the ratio of the electric power output of the solar cell to the light power input. The efficiency is a crucial parameter to estimate the performance of solar cells. Nowadays, there is a quest for surpassing the 50 % solar efficiency, which implies that half of the light coming from the Sun would be transformed into electric power.

Over any other solar cell technologies, the tandem cell with multiple layers or multi-junction solar cell (MJSC) approach is currently the most successful one, as it has held the record of power conversion efficiencies for more than 20 years [4]. Indeed, this is the only approach within the so-called third-generation solar cells that has effectively overcome the Shockley-Queisser efficiency limit (SQ limit) of a single solar cell. Apart from the most considerable efficiencies, MJSCs have some other potential advantages over the Si cells counterparts, such as higher photon absorption for a given thickness (the most widely used materials for MJSC have direct bandgap meanwhile Si has indirect bandgap) which allows thinner and lighter solar cells, and smaller degradation by temperature.

The main drawback of MJSCs cells is that they are significantly more expensive than conventional Si solar cells, for example. There are applications in which other factors, more than price, are the limiting ones, as in the case the space industry, in which maximum efficiency with a minimum device size and weight is required. In these cases, MJSCs are always the best choice. On the other hand, despite the high cell cost, the use of MJSC in terrestrial market applications is worth if the concentration PV approach is used. Concentration technique consists in focusing the sunlight onto the MJSC through lenses or reflective elements to achieve higher light intensities and therefore, increase the power conversion efficiency achieved by the cell. Concentration PV reduces the required collector surface area, which contributes to reduce not only the amount of expensive semiconductor material needed for the cell but also the amount of conventional materials built in the solar module, strongly dropping the cost of energy production. III-V concentrator MJSC are projected to increase their energy production to significant scale levels in the near future, even reaching flat-plate Si solar cells [5].

The latest solar cell efficiency chart published shows that multi-junction technology has reached a 47.1 % efficiency for concentrator devices and 39.2 % for non-concentrator devices with respect to standardized test conditions, direct reference spectrum (AM1.5D) and global reference spectrum (AM1.5G), respectively (Figure 1.2). However, theoretical calculations reveal that if the optimum combination of bandgaps could be achieved, there is still room for a considerable efficiency improvement in multi-junction technology.

Good MJSC performances have been achieved by metamorphic (MM) [6–9], inverted-metamorphic (IMM) [10,11] and wafer bonding [12–15] fabrication techniques, but these approaches imply the use of complex growth techniques and manufacturing procedures. Both MM and IMM approaches employ materials with different lattice constants than the substrate. The strain is relieved during growth by gradually adapting the lattice parameter, growing a thick metamorphic buffer layer between lattice-mismatched junctions. This fabrication process, besides increasing manufacturing costs, can easily promote the formation of dislocations and defects in the material. On the other hand, the wafer bonding technique consists in attaching two different epitaxial structures forming atomic bonds at the interface, and then etching away the corresponding substrates. This technology allows combining lattice-mismatched materials without creating dislocations during growth but requires very low surface roughness, an elaborate specific surface preparation and the use of two different expensive substrates, which considerably increase the cost.

Chapter 1

Since the material quality plays a major role in the cell efficiency and the reduction of fabrication cost is always a pursued goal, monolithic lattice-matched MJSCs cells grown in a single epitaxial step are preferred. Using this technique the different sub-cells maintain a very low-stress level during epitaxial growth [16,17].

Figure 1.2: Solar cell efficiency chart from National Renewable Energy Laboratory (NREL) (taken from ref. [18]).

Indeed, the most extended commercial MJSC is the standard lattice-matched triple-junction $(\text{Al})\text{Ga}_{1-x}\text{In}_x\text{P}(1.9\text{eV})/\text{Ga}_{1-x}\text{In}_x\text{As}(1.4\text{eV})/\text{Ge}(0.66\text{eV})$ structure. Detailed balance limit calculations predict that the efficiency of this cell could be boosted if a 1.0 or

1.15 eV bandgap lattice-matched sub-cell replaces the Ge layer or is inserted between the GaAs and Ge sub-cells [19,20]. Adding this new subcell would allow the optimum bandgap energy combination. The sketches of the projected three- and four-junction cells are shown in Figure 1.3.

Figure 1.3: Sketches of the commercially available MJSC (left) and the projected three- and four-junction solar cells with the 1.0–1.15 eV layer.

Under normal AM1.5G conditions, the calculated solar cell efficiency increases from the 41.4 % of the standard cell to 44.4 % for the three-junction (Al)Ga_{1-x}In_xP(1.9 eV)/GaAs(1.4 eV)/1.0 eV solar cell and to 47.7 % for the four-junction (Al)Ga_{1-x}In_xP(1.9 eV)/GaAs(1.4 eV)/1.0 eV/Ge(0.66 eV) solar cell. Both designs would easily leave behind the 50 % limit when operating under concentration [21–24]. The portion of the solar spectrum used by the standard solar cell and both projected three- and four-junction solar cells is shown in Figure 1.4. The range of photon energies absorbed by the new cells is the same (or even smaller in the three-junction cell) than in the standard cell, but they are more efficiently converted to power. Moreover, the 1.0–1.15 eV layer would be of great interest not only in these novel three- and four-junction sub-cell configurations but even for the future development of five- or six- junction cell designs.

Up to now, the problem has been the lack of suitable, high-quality semiconductor materials to be implemented in these structures. This has led to intensive research trying to produce high-quality semiconductor alloys with a 1.0–1.15 eV bandgap that can be grown lattice-matched to GaAs/Ge. A family of materials that can be potentially used for this purpose are the dilute nitride alloys. Nevertheless, these complex quaternary and quinary

alloys have typically inherent problems that still have to be overcome to push the conversion efficiency of the new MJSCs close to the theoretical limits.

Figure 1.4: Standard AM1.5D solar irradiation spectrum along with energy utilization spectrum calculated theoretically for each sub-cell in a) the standard MJSC, b) a three-junction cell with a 1 eV sub-cell and c) a four-junction cell with a 1 eV sub-cell (taken from ref. [21]).

1.3. Objectives of the Thesis

The main objective pursued in this Ph.D. Thesis consists in developing suitable materials with a 1.0–1.15 eV bandgap that can be grown lattice-matched to GaAs to be implemented as sub-cells in high efficiency MJSCs. We have focused on the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ dilute nitride alloy, which has many potential advantages over the more commonly used $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y\text{:Sb}$, and particularly on GaAs(Sb)(N)-based superlattices (SLs). Since, as far as we know, strain-balanced type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs with high number of

periods have been grown by MBE here for the first time, a significant effort has to be dedicated first to understand their physical properties. The partial objectives of the project cover the whole chain of knowledge from material growth to device fabrication and characterization:

- (1) Growth by Molecular Beam Epitaxy (MBE) and characterization of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ bulk layers lattice-matched to GaAs with the desired bandgap.
- (2) Design, growth by MBE and characterization of different GaAs(Sb)(N)-based SLs with a tailored band structure and 1.0–1.15 eV effective bandgap.
- (3) Extensive analysis of the correlation between optical, electrical and structural properties of samples and the impact of rapid thermal annealing (RTA).
- (4) Device fabrication of 1.0–1.15 eV single-junction solar cells based on these materials.
- (5) Optoelectronic characterization of the fabricated solar cells.

1.4. Structure of the Thesis

Chapter 2 introduces theoretical concepts about PV and solar cell operation and presents background concepts related to semiconductor and dilute nitrides materials, also discussing their possible application in MJSCs. In particular, it introduces GaAsSbN dilute nitride alloy, which has some unique properties that make it a good option for solar cell purposes. This Chapter also introduces two-dimensional structures, especially type-II SLs, and covers the possible implementation of GaAs(Sb)(N)-based SLs in MJSCs.

Chapter 3 summarizes the experimental techniques employed in this Thesis work, covering all steps from epitaxial growth to device characterization.

Chapter 4 presents experimental results concerning optical and structural properties of different GaAs(Sb)(N)-based samples, focusing mainly on type-II SLs. Theoretical simulations on carrier transport and extraction efficiency of SLs with different period thickness are also included in this Chapter.

Chapter 5 presents the solar cell performance of two different series of GaAs(Sb)(N)-based devices consisting in different bulk and SL structures. The first series has relatively “low” N and Sb contents which give rise to ~1.15 eV bandgap; the second series has relatively “high” N and Sb contents which give rise to ~1.0 eV bandgap.

Chapter 1

Chapter 6 discusses the effect of RTA on the luminescence of GaAs(Sb)(N) structures and the solar cell performance of the two series of devices presented in Chapter 5.

Chapter 7 summarizes the most relevant conclusions concerning the results in the Thesis work.

Chapter 8 introduces several different future research directions which would complement the Thesis work.

Appendix A is dedicated to the study of GaAs(Sb)(N) MBE growth conditions and their correlation with the structural, optical and electrical properties of the alloy.

Appendix B includes Tables where the growth parameters of the active layers of all samples that appear in this Thesis are listed.

Appendix C summarizes the theoretical calculation methods employed during this Thesis.

Finally, the Thesis concludes with the list of publications, contributions to conferences and awards related to this Thesis work, and with the Bibliography Section.

2. Theoretical background

2.1. Solar cell fundamentals

2.1.1. The Solar spectrum

The spectral radiation of sunlight mainly consists of visible light, with wavelengths between 400 and 700 nm, and infrared light, with wavelengths from 700 nm to about 2500 nm (see Figure 1.4). However, the solar spectral irradiance on a solar cell (defined as input power received from the Sun divided by unit area and by photon wavelength) is not constant, but depends on several factors: in space, it mainly depends on distance from the Sun; in Earth's surface, it depends on atmospheric conditions and variations, location and position of the cell, and also on the day of the year and the time of the day.

Light-generated current by the cell is proportional to solar irradiance. For this reason, several spectra and power density reference standards have been established to allow an accurate and fair comparison of any reported solar cell efficiency. These standard spectra are represented in Figure 2.1. Air Mass 0 (AM0) ASTM-E490 is the standard spectrum for non-terrestrial use of solar cells [25]; AM 1.5 Global (AM1.5G) ASTM-G173 is the standard spectrum for terrestrial use of solar cells under non-concentrated sunlight, and AM 1.5 Direct (AM1.5D) ASTM-G173 is the standard spectrum for terrestrial use of solar cells under concentration PV [26,27].

The overall power reduction in terrestrial standards is caused by absorption of light by air molecules and dust, which is proportional to the path length that solar light takes through the Earth's atmosphere. AM coefficient is defined as the ratio between the actual optical path length and the shortest possible path length (when the Sun is right at the zenith), and it accounts for this atmospheric absorption effect. Because of this effect, AM1.5 spectra experience an intensity reduction of 18 % compared to the AM0 spectrum.

On the other hand, terrestrial spectra consider light absorption by atmospheric gasses (such as H₂O, CO₂ or O₃), which cause dips in the spectral radiation curves. AM1.5G has larger power in the blue region of the spectrum than AM1.5D because it includes direct radiation (coming directly from the Sun) and diffuse radiation (light scattered by the

atmosphere), while AM1.5D only considers direct radiation. The AM1.5G spectrum is then 10 % more intense than the AM1.5D. AM1.5G spectrum has a real integrated power of 970 W/m^2 , but it has been normalized to 1000 W/m^2 . Thus, the AM1.5D spectrum has an integrated power of 900 W/m^2 .

Figure 2.1: Standard solar spectra for space (AM0) and terrestrial use (AM1.5G and AM1.5D).

2.1.2. Photovoltaic effect and solar cell operation

Solar cells are optoelectronic devices that have been designed and built to collect the maximum amount of sunlight energy when illuminated and directly produce current and voltage to generate electrical power [28,29]. The operating principle of solar cells is based on the photovoltaic effect, discovered by Becquerel in 1839.

Solar cells are commonly diodes based on p-n junctions with certain absorption energy threshold (which is called bandgap energy). The p-n junction consists typically of a semiconductor material with two regions with different doping, one with n-type doping (free electrons available) and another with p-type doping (free hole available). Some of the electrons from the n-type material diffuse to the p-type region and vice versa. Fixed carriers of each material (with opposite sign polarizations) are then exposed, which results in the emergence of an electric field across the interface of the p-n junction, forming the space-charge region.

When a solar cell is illuminated, photons with different energies from the whole solar spectrum arrive at its surface. Only photons with energy equal or exceeding the solar cell bandgap can produce the photovoltaic effect, creating an electron-hole pair. The electric field existing at the space-charge region separates carriers, moving electrons to the n-type side and holes to the p-type side of the cell, preventing electron-hole pair recombination. If both sides of the cell are externally connected, carriers are extracted by the contacts and travel through the circuit, creating a light-generated current flow. The external load counteracts carrier extraction, and a voltage is generated across the solar cell.

2.1.3. Current-voltage curve and solar cell parameters

A current-voltage (IV) curve is the relationship between the electric current that flows through a device and the voltage across its terminal and can be used to study the operation of any electrical circuit. The dark IV curve of an ideal diode (and for extension of a solar cell) follows a non-linear equation:

$$I_D = I_0 [e^{qV/mK_B T_C} - 1] \quad (2.1)$$

Which is called the Shockley diode equation, where I_D is the dark current of the diode, I_0 is the dark saturation diode current, V is the voltage across the cell, q is the electron charge, K_B is the Boltzmann constant, T_C is the operating temperature of the cell and m is the diode ideality factor, which typically take values between 1 and 2. In the dark, when the diode is forward biased, a positive current passes through it, and when the diode is reverse biased, it blocks current except for a small reverse current that is very close to I_0 .

Under illumination conditions, the net current generated by a solar cell that can be supplied to an external circuit is the combination of two currents with opposite signs, the dark current of the solar cell diode (Equation (2.1)) and the light-generated current (I_L):

$$I = I_L - I_0 [e^{qV/mK_B T_C} - 1] \quad (2.2)$$

Where I is the net current through the device. The graphical representation of this equation in the fourth quadrant is known as the IV curve of the solar cell (Figure 2.2).

Some of the parameters used to characterize solar cells are the short-circuit current (I_{SC}), the open-circuit voltage (V_{OC}), the maximum power (P_M) and the fill factor (FF), that are marked in the IV curve graph.

Figure 2.2: Characteristic IV curve of a solar cell. The IV curve is composed of the dark diode current and the light-generated current. The characteristic solar cell parameters are shown in the graph.

2.1.3.1. Short-circuit current

The I_{SC} corresponds to the current through the solar cell when the voltage across it is zero and represents the larger current that the solar cell can provide. The I_{SC} is due to the collection of light-generated carriers; in the ideal case, it is equivalent to I_L (Equation (2.2)). The I_{SC} depends on:

- (1) The area of the solar cell. For that reason, I_{SC} is frequently replaced by the short-circuit current density (J_{SC}), and the IV curves of the solar cells are also usually presented as current density-voltage (JV) curves.
- (2) The spectral irradiance (power and spectrum) of the incident light.
- (3) The optical losses due to absorption and reflection by the solar cell.
- (4) The collection probability of the photogenerated carriers, which depends on the cell active region thickness compared to the diffusion length of the minority carriers, and also on the surface passivation of the device.
- (5) The photogeneration rate. In the ideal case, every photon with energy above the bandgap of the cell produces an electron-hole pair, so the I_{SC} increases as the bandgap decreases.

2.1.3.2. Open-circuit voltage

The V_{OC} corresponds to the forward bias across the solar cell when the net current flowing through it is equal to zero. At that point, the I_L is balanced with the dark current. V_{OC} is the maximum voltage available from a solar cell. In the ideal case, an expression for it can be extracted from Equation (2.2):

$$V_{OC} = \frac{mK_B T_C}{q} \ln \left[\frac{I_L}{I_0} + 1 \right] \quad (2.3)$$

The V_{OC} depends on I_L and I_0 . Since I_0 depends on recombination on the semiconductor material, V_{OC} is a good indicator of the quality of the cell. Moreover, V_{OC} increases with T_C . Unlike in I_{SC} , V_{OC} increases as the bandgap increases, the maximum value attainable being ideally E_{gap}/q , where E_{gap} is the bandgap energy of the solar cell.

2.1.3.3. Maximum power and fill factor

The power delivered by the solar cell is given by:

$$P = I V \quad (2.4)$$

The P_M parameter corresponds to the particular combination of current and voltage for which the power output of the cell reaches its maximum value. Therefore, the ideal operating point of a photovoltaic cell is at the P_M point.

The FF is a measure of the “squareness” of the IV curve, and is defined as the ratio:

$$FF = \frac{P_M}{I_{SC} V_{OC}} \quad (2.5)$$

FF strongly depends on the V_{OC} , so it also relies on the material quality of the cell, and it increases as bandgap increases.

2.1.3.4. Power conversion efficiency

The cell power conversion efficiency (PCE) is defined as the ratio of the P_M to the power of the incident light on the cell. Solar cell performances are usually compared among them in terms of PCE , using solar standard spectra described in Section 2.1.1.

2.1.3.5. Bandgap-voltage offset

Bandgap-voltage offset under open-circuit conditions (W_{OC}) is defined as:

$$W_{OC} = \frac{E_{gap}}{q} - V_{OC} \quad (2.6)$$

Where E_{gap} is the bandgap energy of the cell, and q is the electron charge. This parameter allows comparing the performance of solar cells with different bandgaps in a fairer manner than V_{OC} , as W_{OC} is only slightly dependent on the bandgap of the solar cell [30]. A smaller W_{OC} parameter indicates better cell quality since V_{OC} is closer to its theoretical limit E_{gap}/q .

2.1.3.6. Effect of parasitic resistances on solar cells

In a real solar cell, power is dissipated through resistive effects. The parasitic resistance can be modeled as series resistance (R_S) and shunt resistance (R_{SH}). The diode equation, including these parasitic resistances, becomes:

$$I = I_L - I_0 \left[e^{q(V + IR_S)/mK_B T_C} - 1 \right] - \frac{V + IR_S}{R_{SH}} \quad (2.7)$$

The R_S arises from cell material resistance to current flow, metallic contacts resistance and contact resistance between the semiconductor and the metal. On the other hand, the R_{SH} arises from current leakage through the cell at the edges of the device and between contacts, or from crystal defects or impurities located in the depletion zone [29]. In a good solar cell, the R_S tends to zero; meanwhile, the R_{SH} tends to infinite. The main effect of both parasitic resistances in solar cell performance is decreasing the FF , though very high values of R_S reduces the I_{SC} significantly, and very low values of R_{SH} produce a significant reduction in V_{OC} .

2.1.4. Shockley-Queisser limit, optical losses and third-generation solar cells

Detailed balance limit analysis can predict the maximum theoretical efficiency of a single-junction solar cell. The SQ limit method, first proposed in 1961, is the detailed balance approach most used in PV [31]. The model considers that the solar cell absorbs all photons with energy above the bandgap of the material and that all subsequent hole-pair

recombination cause photon emission, excluding non-radiative recombination. The Sun and the solar cell are modeled as black bodies with temperatures of 6000 K and 300 K, respectively. Figure 2.3 shows the maximum theoretical efficiencies reachable by solar cells depending on their bandgap energy. A crystalline Si solar cell (1.11 eV bandgap) and a GaAs solar cell (1.46 eV bandgap) can provide maximum theoretical efficiencies around 33 %. The maximum *PCE* achievable by a single-junction cell is only slightly more substantial: around 33.5 % for a 1.35 eV bandgap solar cell.

Figure 2.3: Maximum solar cell efficiency under AM1.5G conditions calculated using the SQ limit as a function of the bandgap energy of the solar cell.

Single-junction cells suffer two kinds of loss processes [32–34]. On the one hand, extrinsic electrical and optical losses which make solar cells perform under their SQ limit and could be avoidable by improving the solar cell fabrication. On the other hand, unavoidable intrinsic losses, which are the cause of the low SQ limit values themselves. These fundamental loss processes result in a reduction of either the voltage output or the current output of the cell.

There are two spectral losses mechanisms that are the most significant ones: thermalization or above-bandgap loss, caused by the dissipation as heat of the above-bandgap energy of photons absorbed by the cell because of carrier relaxation to the band minima, which produces a voltage reduction and contributes to cell degradation, and

non-absorption or below-bandgap loss, mechanism responsible of current dropping, as photons with energies lower than the bandgap do not produce photovoltaic effect but are transmitted through the cell. Then, the mismatch between the solar irradiance spectrum and the bandgap energy of the cell is a primary factor of power loss.

Some other losses mechanisms arise on solar cells working at temperatures higher than 0 K, which also impair the power output of the solar cell, but to a lesser extent. Carnot loss is caused by the thermodynamic machine nature of the solar cell device. The solar cell cannot exceed the Carnot efficiency, meaning that the total thermal input cannot be converted entirely into electrical work. Boltzmann loss arises from the fact that sunlight arrives at the solar cell with a solid angle smaller than the emission solid angle. This difference increases the entropy in the cell, which leads to a loss as heat of certain solar input power fraction. Both these mechanisms affect the voltage output of the cell. Losses in the current output come from radiative recombination at the maximum output power condition, which is known as emission loss.

The relative losses caused by the different mechanisms as a function of the bandgap energy of the single-junction cell, along with the maximum power output from the cell (SQ limit) are shown in Figure 2.4. The two main limiting mechanisms degrading the *PCE* of a solar cell are thermalization and non-absorption losses. In a single-junction cell, the reduction of one of these factors means the increase of the other.

Apart from concentration PV, different new-concept approaches have been proposed to try to overcome the SQ limit which affect single-bandgap solar cells, known as third-generation solar cells [35], such as intermediate-band cells, whose concept is based on introducing some energy levels within the bandgap, thus contributing to photon absorption, or hot-carrier cells, consisting on allowing absorption of a wide range of photon energies and then collect the photogenerated carriers before they can undergo a thermalization process . Nevertheless, the technology with a higher degree of development and the only one which has effectively overcome the SQ limit so far is the MJSC technology, already introduced in Section 1.2.

Figure 2.4: Relative importance of the different fundamental loss processes in a single-junction solar cell along with the maximum power output that can be provided by the cell as a function of the bandgap energy (taken from ref. [32]).

2.1.5. Multi-junction solar cells

The MJSC approach [16,21] can to reduce both thermalization and non-absorption losses, taking advantage of a wider part of the sunlight spectrum. In MJSCs, several III-V semiconductor materials with different bandgap energies are stacked, arranged in order of increasing bandgap energy, with the largest bandgap material on top of the cell. Sketches of different MJSCs are shown in Figure 1.3. Each junction or sub-cell can absorb a different section of the solar spectrum, which maximizes the overall photon absorption, so the cell conversion efficiency increases. Absorption of the different segments of the spectral solar irradiance by the different junctions (each junction contribution represented by a different color) of a MJSC is shown in Figure 1.4. Besides non-absorption losses, thermalization losses are also reduced because each photon is absorbed in the junction with bandgap energy closer to its energy.

The different sub-cells of a MJSC are electrically connected in series, which leads to higher output voltage coming from the addition of each sub-cell voltage: the V_{OC} of the MJSC is the addition of those of each sub-cell. Nevertheless, the current produced by a MJSC is limited to the smallest current produced by the constituent sub-cells: the I_{SC} of the MJSC is that of the sub-cell with the lowest I_{SC} . For this reason, a suitable material combination must be chosen to achieve the best current matching between sub-cells.

Theoretically, increasing the number of junctions, as long as they have the optimal bandgap combination, provides a path to larger PCE . This increase in the power output is shown in Figure 2.5, along with the relative losses caused by different mechanisms. To increase the number of junctions is thermodynamically equivalent to increasing the number of engines, so Carnot, Boltzmann and emission losses gradually increases, but both non-absorption and thermalization losses are noticeably reduced.

Figure 2.5: Relative importance of the different fundamental loss processes along with the maximum power output that can be provided by the cell as a function of the number of junctions of the cell (taken from ref. [32]).

Despite this predicted efficiency increasing, nowadays the most efficient commercially available MJSC is the three-junction cell described in Section 1.2. As was discussed in the previous Chapter, the obtention of MJSCs with as the highest possible *PCE* strongly relies on the attainment of a high-quality semiconductor material with a 1.0 or 1.15 eV bandgap that can be grown lattice-matched to GaAs/Ge.

2.2. Dilute nitride semiconductors

2.2.1. III-V semiconductor materials

III-V semiconductor compounds and alloys [36] are commonly used in MJSC engineering. Unlike Si and Ge, most of III-V semiconductors have a direct bandgap, which makes them more suitable materials for optoelectronic applications and devices.

III-V semiconductors are obtained by combining group-III elements (Al, Ga, In) with group-V elements (N, P, As, Sb). The most common binary combinations, together with Ge, are shown in Figure 2.6 as a function of their bandgap energy and their lattice constant.

Figure 2.6: Bandgap energy as a function of the lattice constant of the most common III-V semiconductors: binaries (dots), direct bandgap (solid lines) and indirect bandgap (dashed lines) ternaries, along with Ge. Quaternary dilute nitrides, and particularly $\text{GaAs}_{1-x}\text{Sb}_x\text{N}_y$, can be grown lattice-matched to GaAs and Ge.

Chapter 2

Ternary III-V alloys can be obtained by mixing the binary compounds. Their lattice parameter and their bandgap energy are correlated, as both depend on composition. According to Vegard's law, the lattice parameter of the ternary can be extracted from a linear interpolation of parameters of the constituent binaries:

$$a_{A_xB_{1-x}C} = x a_{AC} + (1 - x)a_{BC} \quad (2.8)$$

Where a_{AC} and a_{BC} are the lattice parameter of the corresponding binaries, x is the molar fraction and $a_{A_xB_{1-x}C}$ is the lattice parameter of the final ternary.

The energy bandgap of the ternary also fulfills the Vegard's law, but sometimes the linear relationship has to be corrected with a non-linear term:

$$E_{\text{gap}_{A_xB_{1-x}C}} = x E_{\text{gap}_{AC}} + (1 - x)E_{\text{gap}_{BC}} - b x (1 - x) \quad (2.9)$$

Where $E_{\text{gap}_{AC}}$ and $E_{\text{gap}_{BC}}$ are the bandgaps of the binary compounds, x is the molar fraction, $E_{\text{gap}_{A_xB_{1-x}C}}$ is the bandgap of the resulting ternary and b is the bowing parameter.

Some of the possible ternary III-V alloy combinations are represented through lines in Figure 2.6. Despite the large number of available binary and ternary III-V semiconductor compounds, there is no any that can be grown with the same lattice parameter than GaAs or Ge in the energy range of interest 1.0–1.15 eV (see Figure 2.6). Then, a non-conventional quaternary or quinary material is required to be used as sub-cell in MJSCs.

III-V quaternary and quinary alloys allow selecting bandgap energy and lattice parameter independently, at least to a certain extent, as they depend on two or more different compositional parameters. For that reason, some of them can have the potential to realize 1.0–1.15 eV solar cells lattice-matched to GaAs.

2.2.2. Dilute nitride semiconductors for 1.0–1.15 eV sub-cell

Among the quaternary materials, dilute nitride semiconductor alloys (like $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ or $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$) arise as leading candidates to be employed in MJSCs as they can fulfill both bandgap and lattice-matching requirements to form the 1.0–1.15 eV lattice-matched sub-cell (see Figure 2.6) [37].

In these highly mismatched alloys, the addition of small amounts (typically less than 5 %) of N in the GaAs matrix leads to an atypically strong bandgap reduction [38], which would allow tuning the bandgap easily to 1.15 or 1.0 eV. At the same time, N reduces the lattice parameter; the fourth element (In or Sb) acts counteracting the tensile strain introduced by N and further reducing the bandgap energy. Thus, the dilute nitride approach enables the obtention of semiconductor compounds lattice-matched to GaAs/Ge with bandgap energies ranging from 0.8 to 1.46 eV (see Figure 2.6).

The giant bandgap reduction caused by the introduction of N can be explained in the framework of the band anti-crossing (BAC) model, as the result of a robust anti-crossing interaction between the localized N-related defect states located above the conduction band (CB) edge of the matrix and the extended CB states of the matrix [39]. Therefore, the CB is split into two sub-bands, E_{CB}^+ and E_{CB}^- , being E_{CB}^- below the matrix CB edge, while the valence band (VB) remains unaffected [40]. Moreover, the new E_{CB}^- has a larger effective mass. Therefore, dilute nitrides show large absorption coefficients due to the increased joint density of states arising from the larger electron effective mass and thus the better matching to the hole band dispersion[41–43].

The dilute nitrides alloys were first proposed in 1996 [44]. Although the considerable efforts devoted to research on $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$, important material and growth-related problems have prevented their implementation as 1.0–1.15 eV material in MJSCs. Up to now, the only successful approach towards the optimum multi-junction design has been the use of $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ in combination with Sb. The surfactant effect of Sb atoms facilitates the two-dimensional growth of the material, attenuating phase segregation and roughening, and reducing the density of point defects [45,46]. The $\text{Ga}_{1-x}\text{In}_x\text{P}/\text{GaAs}/\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y:\text{Sb}$ solar cells fabricated by the Solar Junction CA group have set two consecutive world efficiency records of 43.5 % and 44.0 % under concentration [37,47,48] (see Figure 1.2). These *PCE* records in MJSCs were preceded by strong efforts in optimizing single-junction cells made of $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y:\text{Sb}$ [49]. However, these efficiency values are still well below the theoretical limit, which for concentrator devices overcome 50 %: epitaxial growth and material quality problems inherent to quaternary and quinary dilute nitride alloys lead to low carrier mobility and short diffusion length [50], seriously affecting carrier dynamics [45,51,52]. Despite the intense activity of many groups and some relevant advances [53–60], no improvements in conversion efficiency with three- or four-junction cells have been certified since 2015 [4], and solar cell performance above the 50 % has not been achieved so far [61].

2.2.3. GaAs_{1-x-y}Sb_xN_y for 1.0–1.15 eV sub-cell

GaAs_{1-x-y}Sb_xN_y alloy show important potential advantages over Ga_{1-x}In_xAs_{1-y}N_y, which would allow significant improvement in the current state-of-the-art results. Apart from the Sb surfactant effect, increasing the amount of Sb incorporated would promote a more efficient incorporation of N [62] and reduces the formation of N-related defects [63,64], while eliminating In would avoid the problems induced by the concomitance presence of In and N [65]. All those advantages should lead to a significantly improved minority carrier diffusion length, which is still the main challenge that Ga_{1-x}In_xAs_{1-y}N_y:Sb faces for solar cell applications. Moreover, the reduction of the bandgap energy for the same amount of N is stronger in GaAs_{1-x}Sb_x than in Ga_{1-x}In_xAs.

Also, GaAs_{1-x-y}Sb_xN_y has unusual, unique properties, since it allows an independent tuning of both CB and VB and energies by controlling the N and Sb contents, respectively [66]. This independent control is because, contrary to In, Sb affects mainly only the VB of GaAs [67]. Indeed, the band structure of GaAs_{1-x-y}Sb_xN_y can be modeled by a double BAC (DBAC) model, which is a combination of a CB BAC model for GaAs_{1-y}N_y and a VB BAC model for GaAs_{1-x}Sb_x [68,69]. Moreover, the GaAs_{1-x-y}Sb_xN_y alloy can remain lattice-matched to GaAs if the condition [Sb]≈2.6×[N] is fulfilled [70] since Sb compensates the tensile strain induced by N. A sketch of the GaAs_{1-x-y}Sb_xN_y band structure is shown in Figure 2.7.

Figure 2.7: Sketch of the band structure of GaAs_{1-x-y}Sb_xN_y (blue and red lines) and GaAs (black lines) according to the DBAC model.

The $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ alloy has been recently applied to solar cell technology, both as a thick layer [52,71–84] and as a capping layer over InAs quantum dots [85,86]. Nevertheless, the obtained solar cell performance is not satisfactory up to now. This is due to the fact that $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ still faces important epitaxial growth problems characteristic of the growth of highly mismatched diluted nitrides such as alloy disorder, phase separation because of the large miscibility gap of the $\text{GaAs}_{1-x-y}\text{Sb}_x$ alloy [87,88] that is enhanced with the N incorporation [89], Sb [90] or N clustering [91], difficult compositional control (3 V-group atoms competing for the same lattice position), or N-related point defects and localized electronic states [92–94]. Therefore, achieving a low background carrier density and a long carrier lifetime and diffusion length remains still challenging in this quaternary alloy [49,56].

The only way to overcome growth problems caused by the quaternary nature of the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ alloy is to resort to new growth approaches. Despite of the vast majority of the research efforts dedicated to dilute nitride-based solar cell devices have been centered on thick layers, the outstanding properties of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ alloy, especially the independent control of the CB and VB through the control of N and Sb content, made it a right candidate for band structure and strain engineering, allowing an independent control of electrons and holes. Therefore, apart from bulk layers, nanostructures such as quantum wells (QWs) and SLs with a high versatility in their design can be fabricated with $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$. The use of these low dimensional structures as 1.0–1.15 eV MJSCs layer instead of bulk layers could solve growth-related issues. However, this approach has not been developed up to now.

2.3. Two-dimensional structures

2.3.1. Quantum well structures

In a two-dimensional structure, the motion of the electrons, the holes or both is free in two directions and confined in the other (z -direction). Quantum wells (QWs) are two-dimensional structures in which a thin layer of low bandgap material is sandwiched between two layers of a different bandgap material, forming a heterojunction [95–97]. To start to appreciate quantum confinement effects in a heterojunction, the thickness of the low bandgap layer has to be comparable with the de Broglie wavelength (λ_B) of the electrons or holes:

$$\lambda_B \approx \frac{h}{\sqrt{mK_B T}} \quad (2.10)$$

Where h is the Planck constant, m is the effective mass, K_B is the Boltzmann constant and T is the temperature. In the case of GaAs-based nanostructures, the thickness required to observe quantum confinement at room temperature should be in the range of tens of nanometers or below.

The bandgap discontinuities at the QW interfaces provide the carrier quantum confinement, which leads to a spatial variation in the energy bands of the CV, the BV, or both. Then, electrons and holes can see two different confining potential barriers. In the ideal case of a QW with infinite potential barriers, the possible carrier states inside the well are determined by the Schrödinger equation:

$$-\frac{\hbar^2}{2m_w^*} \frac{d^2\psi(z)}{dz^2} = E\psi(z) \quad (2.11)$$

Where $\hbar$ is the reduced Planck constant, m_w^* is the effective mass of the carriers in the well, z is the growth direction, ψ is the wavefunction and E the energy. Because of the infinite barriers, the ψ is equal to 0 at both well walls. Using these boundary conditions, the analytic solution of the equation is:

$$\psi_n(z) = \sqrt{\frac{2}{d}} \sin \frac{\pi}{d} n z \quad (2.12)$$

Where d represents the well width and n is an integer number. Then, the allowed k values are given by:

$$k = \frac{n \pi}{d} \quad (2.13)$$

So the energy of the confined states (E_n) in the infinite potential well is given by:

$$E_n = \frac{\hbar^2 k_n^2}{2m_w^*} = \frac{\hbar^2}{2m_w^*} \left(\frac{n \pi}{d} \right)^2 \quad (2.14)$$

The existence of quantum confinement gives rise to the existence of a discrete number of energy levels allowed to the carriers, with sinusoidal wavefunctions completely localized within the wells. The energy of the confined states inside the wells is inversely proportional to d^2 , which means that confinement energies are larger for narrow wells and is inversely proportional to the effective mass of the carrier. The confinement energy shifts the effective band edge to higher energy than in an equivalent bulk structure. Moreover, the confinement inside the wells keeps the electrons and holes close together, and hence increases the radiative recombination probability. The existence of confined energy levels also leads to the quantization of the density of states in QWs [97].

In a more realistic QW with finite potential barriers, the Schrödinger Equation (2.11) still described the carrier states inside the QWs, but in the barriers, Schrödinger equation is now:

$$-\frac{\hbar^2}{2m_b^*} \frac{d^2\psi(z)}{dz^2} + V_0\psi(z) = E\psi(z) \quad (2.15)$$

Where m_b^* is the effective mass of the carrier in the barrier and V_0 is the potential barrier height. In this case, the boundary conditions require the ψ to be continuous at well walls. These conditions give a series of even and odd parity solutions:

$$\tan\left(\frac{kd}{2}\right) = \frac{m_w^*\kappa}{m_b^*k} \quad (2.16)$$

$$\tan\left(\frac{kd}{2}\right) = \frac{m_b^*k}{m_w^*\kappa} \quad (2.17)$$

The Equations (2.16) and (2.17) have to be solved numerically. The energy of the confined states obtained is:

$$E_n = \frac{\hbar^2 k^2}{2m_w^*} \quad (2.18)$$

$$V_0 - E_n = \frac{\hbar^2 \kappa^2}{2m_b^*} \quad (2.19)$$

Where κ is the exponential decay constant in the barrier. In this case, the wavefunctions are approximately sinusoidal inside the well, but they extend to the barriers where they decay exponentially depending on the finite potential barrier height. E_n are smaller than those of the infinite well due to the reduced confinement of the wavefunctions. However, the energy of the confined states also increases when the QW thickness is reduced.

2.3.2. Superlattice structures

In a periodically repeated multi-QW (MQW) structure, a similar approach to find the allowed energies for the carriers than that of the previous Section can be used, changing the boundary conditions to take account of the structure periodicity. The Kronig-Penney model can be applied [98], due to the similarity of the MQW to a two-dimensional crystal lattice, along with the Bloch wavefunction formalism. The allowed energy has to be calculated numerically.

For certain barrier thickness, the obtained solutions reveal the existence of discrete allowed energy bands separated from each other and with wave functions localized within the wells. For barriers thin enough, the wave functions in neighboring wells can be coupled through the barriers. In this case, the structure becomes a SL: the discrete energy levels broad into minibands and the wave functions are delocalized throughout the whole structure [99,100].

The width of each miniband depends on the strength of the electronic coupling through the barriers, which is determined by the barrier thickness, the potential barrier, the decay constant and the effective carrier mass [97]. In general, the higher energy states give rise to broader minibands because the decay constant decreases with E_n . Also, the hole minibands are narrower than the electron minibands, because the coupling decreases with increasing effective mass. A schematic diagram of a QW and its evolution into a SL after electronic coupling is shown in Figure 2.8.

Figure 2.8: Diagram of a QW and a SL. Confined states are shown in the sketch of the QW. Because of the electronic coupling, minibands are formed in the SL from the energy levels of the corresponding QW.

This reduction in the SL carrier confinement concerning QW results in different SL carrier conduction mechanisms [100,101], which depends on the carrier coupling through the barriers. The important for this Thesis are:

- (1) Miniband transport. For highly coupled SLs, carrier transport mainly occurs through the miniband. When scattering is negligible, carriers can even undergo ballistic transport, meaning that the mean free path of the electron is longer than the distance traveled through the SL.
- (2) Sequential resonant tunneling. In weakly coupled SLs, the miniband transport is not applicable. In this case, under the application of an external electric field, band bending can lead to the coupling of different-level confined states from adjacent wells provide that the potential drop is equivalent to the energy spacing of the bound states. Coupling of equivalent confined levels can occur for broaden confined states, or through phonon-assisted tunneling.
- (3) Thermionic scape transport. In weakly coupled SLs inside a p-i-n junction, photogenerated carriers can be trapped in the well have the chance of overcoming the potential barrier and escape due to the finite thermal energy, contributing to the current.

2.3.3. Types of band alignment

Depending on the relative positions of the bandgaps of the constituent layers, the QWs can have type-I, type-II or type-III band alignment. In a type-I band alignment, the bandgap of one of the materials is within the bandgap of the other: electrons and holes are confined inside the material with narrower bandgap. In a type-II band alignment, only one of the bands (CB or VB) of one of the materials is within the bandgap of the other: electrons are confined in one of the materials but holes in the other. Finally, in a type-III band alignment, both VB and CB of one of the materials are located outside the bandgap of the other material. A scheme of the two kinds of alignments used in this Thesis, type-I and type-II, is shown in Figure 2.9.

Figure 2.9: $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$ MQW with type-I band alignment and b) $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ MQW with type-II band alignment. The distribution probability of the wavefunction is represented in blue for electrons and red for holes.

Type-II band alignment in QWs provides a long radiative carrier lifetime that should reduce carrier recombination and enhance carrier escape [102]. Due to these potential advantages, SLs with this kind of band alignment have experienced a rapid development for IR detection [103,104] and solar cell applications [105]. Nevertheless, in the case of the SLs, the situation might not be so simple. Strong electronic coupling resulting in miniband formation would in principle reduce the carrier lifetime since the electronic structure becomes more type-I like when the wavefunctions delocalize. Therefore, a strong correlation between carrier lifetime and electronic coupling (and, therefore, carrier transport) exists, which would be ultimately determined by the period thickness. This correlation, however, has been typically masked in the well-studied InAs/(In)GaSb and related SLs developed for mid IR detection, in which carrier lifetime is in general dominated by Auger recombination [106,107], or has frequently been omitted in studies in which a

long carrier lifetime is reported using very thick periods, which could make the structure useless for device applications in which good carrier transport is required [108]. We think that GaAsSb/GaAsN type-II SLs constitute a unique system to study this correlation: the larger bandgaps make the relative weight of Auger recombination negligible, and, besides, it allows an independent tuning of electron and hole electronic coupling.

2.3.4. Quantum wells and superlattices for solar cells

Since the use of QWs in photovoltaics was first proposed [109], QWs have shown great potential for the realization of more efficient MJSCs. The QW layers grown within the depletion region of a p-i-n solar cell provide a means to engineer the absorption edge of solar cells [110]. Limitations have been demonstrated in strained MQWs systems [111], but in strain-balanced MQWs in which strain does not cause formation of dislocations, higher J_{SC} values and conversion efficiencies compared to an equivalent bulk solar cell with the barrier bandgap have been demonstrated [112,113], also in MJSCs [110,114–116]. Therefore, obtaining strain-balanced MQW structures is a critical issue for developing efficient QW solar cells [111,117,118].

However, the advantages provided by MQW solar cells can be suppressed because of an inefficient carrier collection process: the carrier extraction from and transport across the MQW structure may be hindered due to carrier confinement, which leads to recombination of the photogenerated carriers [119], also degrading the V_{OC} [120].

These carrier collection problems could be solved by promoting electronic coupling between the QWs, i.e., transforming the MQW structure into a SL. In this case, the formation of minibands would actively facilitate carrier transport across the structure [120]. As described in the previous Section, a type-II band alignment could give rise to enhanced carrier collection efficiency, so type II SL structures are particularly interesting to be investigated regarding possible application of QW-like structures in MJSCs.

Regarding dilute nitride QWs, GaAs_{1-y}N_y/GaAs and Ga_{1-x}In_xAs_{1-y}N_y/GaAs MQWs have been proposed [121] and already grown for solar cell applications [122,123]. Also GaAs_{1-y}N_y/InAs_{1-y}N_y, GaAs_{1-y}N_y/GaAs_{1-x}Bi_x and GaAs_{1-x-y}Bi_xN_y/GaAs SLs have been proposed as suitable structures for photovoltaic applications [124–126], and GaAs_{1-y}N_y/Ga_{1-x}In_xAs SLs have already been experimentally realized [127].

2.3.5. GaAs(Sb)(N)-based superlattices for 1.0–1.15 eV sub-cell

GaAs(Sb)(N)-based SLs can be grown strain-balanced and lattice-matched to GaAs. They can be fabricated with type-I band alignment, alternating layers of quaternary $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ with GaAs barriers, but also with type-II band alignment, alternating layers of the ternaries $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-y}\text{N}_y$ (see Figure 2.9). Electrons are always confined in N-containing layers. Meanwhile, holes are always confined in Sb-containing layers. Moreover, the position of CB and VB of the layers would depend on the amount of N and Sb introduced in the matrix (see Section 2.2.3.).

GaAs(Sb)(N) SLs have some advantages over the equivalent bulk material. On the one hand, they make it possible to reproduce the bandgap energies of the quaternary alloy using only half the amount of Sb and N. An overall reduction of the N content should result in an overall reduction of N-related defects in the structure and, therefore, an improved crystal quality. On the other hand, their effective bandgap does not only depend on N/Sb contents but also on an extra parameter: SL period and relative thicknesses of the layers. This fact would allow tailoring the band structure and the effective bandgap to optimize device performance.

Furthermore, specifically type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs offer the advantage of spatially separating N and Sb atoms, which could lead to reduce some of the typical miscibility problems of the dilute nitride alloys. Moreover, electron and hole electronic coupling can be independently tuned in these structures by the N and Sb content, respectively.

Despite all the potential advantages of GaAs(Sb)(N)-based SLs for its application to MJSCs, as far as we know, this approach has not been investigated, and the structures have never been grown.

3. Experimental techniques and methods

In this Chapter, the main experimental techniques and methods employed during this Thesis are described, from the epitaxial growth (Section 3.1) and material characterization (Section 3.2), right through to the subsequent device fabrication (Section 3.3.) and device characterization (Section 3.4.). The procedure to apply RTA cycles is also described (Section 3.5.).

3.1. Epitaxial growth: Molecular beam epitaxy

Molecular beam epitaxy (MBE) is an epitaxial thin film growth technology. In the MBE process, beams of atoms or molecules coming from elemental materials sources are directed toward a heated crystal substrate inside a vacuum chamber which bare pressure is in the ultra-high vacuum (UHV) range (from 10^{-8} to 10^{-11} Torr). UHV conditions make the atom beams travel in collision-free paths. Thermal energy causes impinging atoms to migrate over the substrate surface to lattice sites and conform thin layers of very high purity crystal which structure depends on the underlying substrate structure and which composition can be rapidly and accurately controlled. If the deposited thin film has the same lattice constant as the substrate and similar thermal lattice expansion coefficients, the whole structure is grown lattice-matched.

This thin-film growth approach emerged at the end of the 1960s [128–130] and has been strongly developed since then as it can be used to grow layer-by-layer a broad range of ordered and tailored materials, especially III-V semiconductors like GaAs and related compounds. The development of the MBE technique has opened the door to exploit the advantages of SL structures with layer thickness in the range of monolayers (MLs) [131], as that kind of nanostructures typically requires layer-by-layer growth control with high structural perfection and high interface control. Furthermore, the strain-balance control achieved through the MBE technique allows the growth of SL structures containing many repeated periods. Basics of MBE technique have been described and reviewed in numerous published works [132–134].

Chapter 3

All samples in the Thesis were grown with a MBE system located in the cleanroom of the Institute for Systems based on Optoelectronics and Microtechnology (ISOM). This MBE system is composed of three chambers: a Riber 32 MBE growth chamber, an intermediate chamber that is equipped with an Ar ion beam for controlled dry etching, and an introduction chamber. Each one of the chambers relies on an independent pumping system and is isolated from others through gate valves that are only opened during the transfer process, to avoid contamination and to maintain the pressure into the growth chamber as low as possible. A global view of the ISOM MBE for III-As compounds system is shown in Figure 3.1.

Figure 3.1: MBE system located at ISOM cleanroom.

The substrates used to grow samples in this MBE are pinned in an In-free Moly-block substrate holder and loaded into the system through the introduction chamber, which is subsequently pumped down. The vacuum is obtained in a first step through a rotatory pump plus a turbomolecular pump system, and then an ionic pump comes into play. Thanks to a heating filament, substrates are outgassed for two hours to eliminate dirt particles and water molecules from the substrate surface before transferring them through the intermediate chamber to the growth chamber.

The growth chamber is the essential element of any MBE system; a diagram of a typical MBE growth chamber is shown in Figure 3.2. Uniquely, for respect to the Riber 32 growth chamber used for the present Thesis work, it is equipped with Knudsen effusion cells for Ga, In, Al, Sb, and also Be and Si (that are used as n-type and p-type doping sources). These materials are placed inside a Pyrolytic Boron Nitride (PBN) crucible, which can withstand high temperatures. The growth chamber also counts with an As_4 source equipped with a cracker, which can split the As_4 into As_2 and a needle valve which allows high precise flux control. Although the cracker is not used in this Thesis (we grow with As_4 and not As_2) it is always heated to a higher temperature than the arsenic reservoir to avoid the condensation of As_4 molecules before entering the growth chamber. All the source elements employed have extremely high purity: 99.999995 % in the case of Ga, In, Sb and As_4 , 99.99995 % in the case of Al and 99.99+ % in the case of Be. Si employed is fabricated by the float zone (FZ) process, which guarantees high-purity monocrystalline Si with negligible O_2 contamination.

Figure 3.2: Schematic diagram of a MBE growth chamber; the main experimental elements are shown (adapted from ref. [134]).

The MBE source cells are geometrically arranged in the growth chamber so that the distance and solid angle to the sample holder is roughly equal for all of them. The cells are heated up at elevated temperatures before growth, and the material inside them is evaporated

or sublimated, which provide the molecular beams of materials. The heating temperature of each cell is proportional to the beam material flux. In the particular case of III-V semiconductors growth, V-group elements (As and Sb) are much more volatile than III-group elements (Ga, Al and In). For this reason, the setting cell temperatures of III-group elements are considerably higher than V-group elements ones. A set of mechanical shutters located in the front of the cells can be closed or opened to interrupt or resume the arrival of the material fluxes to the substrate.

The Riber 32 MBE allows growing of dilute nitride materials because it is equipped with an ultra-pure N₂ line and an Oxford Instrument nitrogen radio frequency (RF) plasma source. A flow of pure N₂ obtained from a high purity bottle (99.99995 %) flows through a mass flow controller (MFC) which provide an exact 0.1 SCCM flow. The ultra-pure N₂ line is fitted with its turbomolecular pump to avoid contamination. The N flux is injected in the RF plasma through two metallic valves, and cracked in different reactive N species, containing neutral and charged molecular and ionic and neutral atomic, along with free electrons, after application of an ignition 13.56 MHz RF power. Atoms produced in the discharge have to pass through a beam aperture plate which consists of an array of 21 holes of 25 mm-diameter. An optical emission detection (OED) system tuned to the characteristic emission line of the atomic N is monitored, which is proportional to the N flux. The OED value is directly related to the N₂ gas flow provided to the source and the RF power applied; these parameters are related to the content of N incorporated during growth. A hermetic valve placed behind the plasma source complement the role of the N shutter providing accurate control over N flux, avoiding the presence of N background in the structure and confining it on their corresponding layers.

The growth chamber is equipped with a quadrupole mass spectrometer that can detect the presence of atoms or molecules inside the chamber, giving information about the environment in which samples are grown. The growth chamber is also equipped with a reflective high-energy electron diffraction (RHEED) system for in-situ characterization of growing samples, which design and functionality would be specifically described in Section 3.1.1.

UHV is created in the growth chamber with two kinds of pumps, an ion pump and a closed-cycle cryogenic pump. Moreover, growth chamber walls are surrounded by a cryo-panel where liquid nitrogen flows during growth. Liquid nitrogen reduces the temperature of the cryo-panel, which trap impurities and contributes to create the UHV regime. During the growth of dilute nitrides, the pressure inside the growth chamber raises to 10⁻⁵ Torr.

Samples mounted on the substrate holder and transferred to the growth chamber are placed in a holder manipulator. The manipulator is rotated 180° to make the substrate face the element beams. The manipulator can also turn continuously around the plane normal to the substrate, which is necessary during the epitaxial process to ensure steady growth. A heating filament in the back of the substrate provides the thermal energy necessary for the diffusion of arriving atoms on the substrate surface. In MBE growth, there is an interplay between cell temperatures and substrate temperature: for each incident rate of arriving particles, there is a critical substrate temperature which enables epitaxial growth and vice versa.

Before the growth process starts, the beam equivalent pressure (BEP) of each material flux can be measured using a Bayard-Alpert ionization gauge placed on the holder manipulator. Such pressure is proportional to the number of atoms arriving at the sample surface, so it is useful to control the sample composition. In the III-V MBE growth, elements with very different vapor pressure are combined: group-V elements are much more volatile than group-III elements, they are thus easier to desorb. All the samples have been grown under overpressure of group-V element (As_4) to assure correct deposition; meanwhile, the flux of the group-III element (Ga) determines the deposition growth rate.

3.1.1. RHEED: in-situ characterization during epitaxial growth

The MBE growth chamber is equipped with an in-situ characterization tool that can provide real-time information about surface roughness, surface order, surface orientation, growth rate, growth mode of the sample and even polycrystalline grain size during growth process of epitaxial solids. The technique is also used to determine growth temperature with reasonable accuracy. RHEED technique was introduced in GaAs MBE systems at the very beginning of the MBE technique [135] and is widely discussed in [133].

The basics of the RHEED system (Figure 3.3) consists in a high-energy electron beam that is emitted by an electron gun and strike the sample at very low glancing angle (from 1° to 3°). There, electrons are diffracted and finally reach a fluorescent or phosphorescent window screen where a diffraction pattern is formed. The minimal angle between the electron beam and the sample surface is a determinant factor for the RHEED technique, as it prevents the electrons from reaching sample material beyond the first atomic layers, which ensures that the diffraction pattern observed in the screen to be indicative of the atomic arrangement at the sample surface.

On the one hand, the appearance of the diffracted features can be used to monitor the quality of the deposited layers. If the growing surface is amorphous, the diffraction condition cannot be achieved, so a diffuse pattern is observed in the RHEED screen. On the other hand, if the growth front is flat, the electrons undergo coherent diffraction by sample surface, and then the observed features have a streaky pattern, meanwhile a growth surface with certain roughness gives rise to a spotty diffraction pattern, as electrons are not only diffracted by surface but transmitted through surface island structures.

Figure 3.3: Schematic diagram of RHEED geometry, where θ is the glancing angle, Φ the azimuthal angle, L is the distance between the point of incidence of the beam and the fluorescent screen and W indicates the spacing among spot features in the screen (taken from ref. [134]).

RHEED tool is also useful to accurately calibrate the growth rate of the deposited material. The fundamentals of this process are shown in Figure 3.4. If the growth mode is an ideal layer-by-layer, which involves nucleation and subsequent growth and coalescence of two-dimensional islands on atomically flat terraces, the intensity of the diffracted spots in RHEED pattern oscillates periodically during growth [136,137]. The oscillation period corresponds to the time needed for a single ML to growth: When the sample surface is atomically flat because a ML is completed, diffracted beams are coherent and the intensity observed in the screen is maximum. When the islands of the next ML start to grow, signal intensity starts to decay, reaching a minimum when half of an epitaxial ML is formed on the surface. In the case of the GaAs(Sb)(N) samples grown for this Thesis work, the growth rate is determined by the III-group flux (Ga) as at the usual growth temperatures ($\sim 580^\circ\text{C}$

and $\sim 470^\circ\text{C}$) it has a sticking coefficient of 1, so the growth rate determined by RHEED oscillations is proportional to the Ga cell temperature.

Figure 3.4: Sketch showing the layer-by-layer growth of a complete (001) GaAs single monolayer (left column), the diffraction of the electron beam by the sample surface, where $\bar{\theta}$ is the fractional layer coverage (center column), and the corresponding RHEED signal intensity (pointed with a dot) for each $\bar{\theta}$ (right column) (taken from ref. [137]).

However, in practice, the oscillations do not go on indefinitely but amplitude decay remarkably after a few periods. Figure 3.5 shows a real diffraction intensity oscillation signal taken during the growth of a GaAs buffer layer, where such a phenomenon is observed. This decay happens because epitaxial growth is not exactly an ideal layer-by-layer growth, but after the partial growth of one ML on the surface, a second layer would nucleate before the previous one is complete, which leads to the formation of an increasingly rougher surface, reducing the maximum intensity until finally, the oscillating behaviour disappears [138].

The observation of RHEED oscillations during the growth of all samples of this Thesis assesses their layer-by-layer growth mode. Apart from this classical growth mode, the

step-flow growth mode could give rise to two-dimensional nanostructures with abrupt interfaces [139]. This growth mode can take place on surfaces with monatomic steps composed of terraces and edges. For a high enough diffusion length (usually achieved at very high temperatures) the arriving adatoms can migrate to the existing step edges before nucleation occurs on the terraces. Since RHEED intensity oscillations occur as the result of the formation of 2D island in the flat surface, in the step-flow growth process, RHEED oscillations are not observed [140,141].

The RHEED intensity graphs of this Thesis, as the one shown in Figure 3.5, are obtained using a software program that analyzes the light intensity in a selected area of a video recorded with a digital camera placed over the RHEED screen.

Figure 3.5: *RHEED intensity as a function of time measured during the growth of a GaAs layer. A growth rate of 1.1ML/s can be deduced by dividing the number of oscillation periods by the time.*

On the other hand, the number, intensity and spacing of the RHEED diffracted features are directly related to the arrangement of the atoms in the two-dimensional unit cell on the surface of the material (called surface reconstruction), which pursues minimizing the surface energy. The same material has different surface reconstructions for each crystallographic plane orientation, depending on the constituent element fluxes and the substrate temperature. Therefore, the RHEED pattern observed allow identifying the crystal

orientation and the surface reconstruction of the growing material. Moreover, as long as the used beam fluxes are known, monitoring RHEED surface reconstruction transitions provides a method to calibrate the growth temperature [142].

Most of the III-V semiconductors, including the GaAs, have zinc blende structure, with III-group and V-group atoms planes alternating along the [001] direction. The ideal GaAs (001) surface has two dangling bonds for each surface atom. Depending on the surface stoichiometric and composition these dangling bonds can be reorganized in several ways giving rise to different surface reconstructions such as $c(4 \times 4)$, (2×4) , (6×6) , $c(8 \times 2)$ or (4×6) , for example.

Taking all of this into account, in the samples of this Thesis work two different surface phenomena have been used as reference for growth temperature determination. On the one hand, when native oxide decomposes from the GaAs surface at $\sim 580^\circ\text{C}$, RHEED image switch from a diffuse pattern, typical of the rough amorphous oxide layer, to a spotty (2×4) diffraction pattern, typical of an ordered As stabilized (001) GaAs surface. On the other hand, under As_4 overpressure conditions, the (001) GaAs surface undergoes a phase transition at $\sim 510^\circ\text{C}$. At that temperature, the RHEED pattern shows the change from a (2×4) to a cubic As-rich (4×4) reconstruction [143]. Both surface reconstruction patterns are shown in Figure 3.6.

Figure 3.6: RHEED diffraction pattern of GaAs surface showing a) (2×4) the surface reconstruction, taking at $\sim 580^\circ\text{C}$ and b) the $c(4 \times 4)$ surface reconstruction, taking at $\sim 490^\circ\text{C}$.

3.1.2. Growth details of samples in the Thesis

All samples grown during this Thesis have the same basic epitaxial structure. The substrates used are quarter pieces taken from 2-inch diameter GaAs (001)-oriented Si-doped (GaAs n^+) wafers, which have a thickness of 250 μm . Such substrates are outgassed in the introduction chamber at $\sim 350^\circ\text{C}$ for two hours before the growth process.

As the first step of the growth process itself, the GaAs substrate temperature is raised to $\sim 620^\circ\text{C}$ to desorb the native oxide coating. At the same time, As_4 flux is introduced into the chamber to avoid As desorption from the sample surface; samples are grown under As_4 overpressure. When the amorphous layer of native oxide is eliminated, which is indicated by a RHEED pattern change from a blurred to a clear spotty configuration, the substrate temperature is slightly lowered to $\sim 580^\circ\text{C}$, and then a “smoothing” GaAs layer is deposited. This layer consists of 3 repetitions of the following: four 10 ML-thick GaAs layers separated each other by 10 seconds of growth interruption. The next deposited layer is a 250 nm-thick GaAs buffer layer also grown at $\sim 580^\circ\text{C}$. The $\sim 580^\circ\text{C}$ temperature was selected because it is inside the optimal temperature range for growing high-quality GaAs. Subsequently, the growth temperature is reduced to $\sim 470^\circ\text{C}$, at which the active layer of the sample is grown. This $\sim 470^\circ\text{C}$ temperature is specially optimized for the growth of N-containing samples, as it guarantees high N incorporation [144]. The active layer consists of a 200 or 816 nm-thick undoped GaAs(Sb)(N) layer whose growth rate is comprised between 1 and 2 ML/s. The active layer can specifically consist on thick layers of the ternaries $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-y}\text{N}_y$, thick layers of the quaternary $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$, or SL structures fabricated with type-I band alignment, stacking alternate layers of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ and GaAs, or with type-II band alignment, stacking alternate layers of $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-y}\text{N}_y$ (see Figure 2.9).

The N and Sb contents to be incorporated in the active layers are approximately between 1 and 2.5 % in the case of the N (dilute nitride alloy regime) and between 3 and 6.5% in the case of the Sb. In these content ranges, the thermal expansion does not play an essential role in the homoepitaxial growth of lattice-matched GaAs(Sb)(N) layers over GaAs. On the other hand, to adjust in each case the Sb and N fluxes required to provide the desired composition, two series of $\text{GaAs}_{1-y}\text{N}_y$ and $\text{GaAs}_{1-x}\text{Sb}_x$ ternary samples were grown at the beginning of this Thesis work. These series allowed the careful calibration of the N and Sb incorporation in the ternary alloys as a function of the OED and Sb BEP, respectively. This calibration is shown in Appendix A. Finally, the growth temperature is raised again to $\sim 580^\circ\text{C}$, and a 50 nm-thick capping GaAs layer is deposited on top.

Samples with a 200 nm-thick active layer are grown to study the growth process and to test the structural and optical properties of each structure through material characterization. Samples with a 816 nm-thick active layer are grown for further solar cell processing and characterization. In the thicker samples, the buffer layer is n-type doped during growth, and the top capping layer is p-type doped. Both n- and p-type doping have a nominal concentration of $2 \cdot 10^{18} \text{ cm}^{-3}$. The sample configuration is, therefore, a p-i-n junction, with the active GaAs(Sb)(N) layer as the intrinsic layer.

However, this epitaxial structure is not optimized for single-solar cell devices, as the purpose of this Thesis work is mainly comparative. The addition of a passivating window layer on top of the cell, a back-surface field (BSF) layer at the bottom of the absorbing active layer, or both, would allow a significant improvement of the solar cell performance. The window layer prevents electron recombination in the front surface of the cell, which profoundly affects J_{sc} [145,146]. In GaAs-based solar cells, AlGaAs or InGaP epitaxial layers are typically used as window layers due to their wide bandgap energy and appropriate lattice parameter. On the other hand, a BSF layer helps to achieve high V_{oc} and thus high efficiency by preventing hole recombination and contributing to confinement of the photogenerated carriers within the p-n junction, without increasing the series resistance [147,148]. In GaAs-based cells, this layer usually consists of an AlGaAs layer at the back of the cell. Moreover, neither the thicknesses nor the doping concentrations of the different layers (including the active layer) are optimized. Finally, the grown structure also lacks a heavily doped p^{++} thin contact layer on top of the cell.

The active layer structures of each set of samples are described at the beginning of each corresponding Section. Furthermore, the growth details of the active layer of all the samples are summarized in Appendix B.

3.2. Material characterization

Material characterization allows correlating the sample growth conditions with the structural, optical and electrical properties of the alloy, and systematically determining the influence of different structure designs and various growth conditions on the quality of the grown layers and the N and Sb incorporation. Material characterization is divided into two branches: optical characterization, including photoluminescence (PL) spectroscopy, time-resolved photoluminescence (TR-PL) spectroscopy and photoreflectance (PR) spectroscopy, and structural characterization, consisting on X-ray diffraction (XRD) and Transmission electron microscopy (TEM).

3.2.1. Photoluminescence spectroscopy

PL spectroscopy is one of the leading optical characterization techniques in semiconductors, among other things because it is a non-destructive technique that does not require any special sample preparation. The PL spectroscopy has been extensively reviewed in numerous published works [149–151].

In PL experiments, a semiconductor sample is excited with a light source, usually a laser with a photon energy higher than the bandgap of the material. After photon absorption, electron-hole pairs are created that afterward typically undergo Coulomb scattering or phonon interaction and relax to the band minima before recombining. The electron-hole recombination can be a radiative or a non-radiative process; if recombination is radiative, photons are emitted, and a PL signal can be detected.

To begin with, the intensity of the PL emission provides some insight into the material quality. A high intensity of the PL peak points to an efficient radiative recombination; meanwhile, a reduced PL intensity is often related to stronger Shockley-Read-Hall (SRH) non-radiative recombination processes, usually associated to the existence of defects or impurities in the material.

Radiative recombination that gives rise to PL signal can have a different origin. On the one hand, free-carrier recombination or band-to-band recombination occurs at energies higher or equivalent than bandgap energy; the PL peak energy of the band-to-band recombination can be considered, as a first approach, to indicate the effective bandgap of the sample. Nevertheless, the PL peak energy could be shifted to higher energies in QWs or SLs when using high excitation power due to band filling effects, or to lower energies if excitonic recombination is present. The existence of extrinsic defects in the semiconductor structure also can give rise characteristic PL signal, typically associated with donors, acceptors, or deep levels within the forbidden gap of the semiconductor.

The full width at half maximum (FWHM) of the PL peaks is a parameter of interest: a broadening could indicate some fluctuations in the material bandgap energy which could be related to alloy disorder or interface roughness. Integrated intensity (II) is another parameter of interest that can be related to the origin of the radiative recombination.

Low-temperature (15 K) PL measurements have been systematically performed on the grown samples of this Thesis using the infrared PL measurement setup that is located in the ISOM optic laboratory. A schematic diagram of the setup is shown in Figure 3.7. The incident photons are emitted out from a He-Ne laser (632.8 nm wavelength) with a power

of 3 mW that can be attenuated by a neutral density filter. The laser beam, modulated at 25 Hz using a chopper placed as near as possible to the laser, is directed through an optical path comprised of a series of lenses and mirrors to the sample, which is mounted in a cryostat system that is cooled down using closed-cycle He in high vacuum conditions.

The PL signal emitted by the sample is focalized and filtered to avoid second-order effects before going through a 1-m focal length spectrometer, where it is dispersed. The intensity for each wavelength is detected using a liquid-nitrogen cooled Ge-detector. Signal is amplified with standard lock-in techniques at the chopper frequency to increase the signal-noise ratio of the PL spectrum, and finally recorded using a computer.

Figure 3.7: Diagram of the infrared PL setup used at ISOM.

3.2.1.1. Photoluminescence spectroscopy on dilute nitrides materials

In dilute nitrides materials, the introduction of a few percent of N into the host matrix causes a substantial impact on the material properties. N incorporation causes composition inhomogeneities in the alloy [94,152,153] (which in the case of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ can be partially relieved because of the Sb surfactant effect) and can lead to the formation of N-rich clusters and N-interstitials [154,155] or other kinds of point defects [52,54,83,93,154,156–158]. Composition inhomogeneities and N-related point defects contribute to create carrier

localization effects and non-radiative recombination centers [190–193], which are commonly observed in dilute nitrides with N content above a certain threshold.

All these effects have a significant influence in the PL spectra. In $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ [159–163], $\text{GaAs}_{1-y}\text{N}_y$ [164–166] and $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ [167,168] dilute nitrides, the band-to-band PL energy peak redshifts when N is introduced in the material, at the same time than the PL intensity rapidly decreases and the FWHM increases. These phenomena are proportional to the N concentration. The redshift observed is related to the amount of N in the alloy, accounting for the large bowing parameter at low concentration [159,168]. On the other hand, the considerable local strain introduced by the small N atoms make the crystallinity of the material worse [159]. Moreover, the low temperatures at which the N-containing materials are usually grown to favor N incorporation contribute to a large density of point defects and reduced structural quality, giving rise to a high non-radiative recombination and degraded PL [164].

An exponential-like tail at low energies of the band-to-band PL peak is also usually observed in $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ [159–161,163,166,169–171], $\text{GaAs}_{1-y}\text{N}_y$ [164–166] and $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ [167,168], given to the PL peak an asymmetric lineshape. This tail is attributed to a localization effect attributed mainly to random fluctuations of alloy compositions [161,166,170,171]. The slope of the PL tail can provide some qualitative information about the fluctuation potential responsible for the exciton localization. A typical PL spectrum of a dilute nitride sample is shown in Figure 3.8.

Figure 3.8: Typical PL spectra of a dilute nitride material, with a highly asymmetrical band-to-band PL peak.

The deterioration of the optical properties in dilute nitrides can significantly affect the solar cell performance. Typically, the poor photovoltaic performance of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ has been attributed to the presence of non-radiative recombination centers, and the improvements achieved have been linked to their reduction. In our case, the increment of N concentration to the values necessary to reach bandgap energies around 1.0–1.15 eV (those required for layers intended for MJSCs) are enough to face significant carrier localization effects and non-radiative recombination.

3.2.2. Time-resolved photoluminescence spectroscopy

Time-resolved photoluminescence (TR-PL) spectroscopy is a non-destructive luminescence technique that provides the evolution of the PL intensity as a function of time for a fixed wavelength, after being illuminated by a short pulse of light. Only direct bandgap semiconductors can emit enough light to be suitable for TR-PL [172]. The PL intensity is proportional to the rate of radiative recombination, which in turn is proportional to the number of minority carriers. Therefore, the decay time constant is also called the minority carrier lifetime.

The decay of the excess of electrons and holes photogenerated after the incident pulse of light typically follows an exponential transient. The lifetime of the minority carrier depends on the recombination centers existing in the material. If more than one recombination center with different decay rates have a role in the luminescence, the exponential transient obtained can have different slopes in different regions.

Thus, TR-PL allows monitoring minority-carrier recombination and their corresponding lifetimes, even if this recombination is due primarily to a non-radiative mechanism, as they also influence the exponential decay. The typical TR-PL decay times in semiconductors are on the order of pico- or nanoseconds, and the intensity of the emitted light can be very weak, so the use of a high-resolution detection system such as the single-photon counting technique is required.

In this Thesis work, this technique has been used to investigate the recombination mechanisms in SLs structure and to confirm the type-II band alignment in $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs, since it should result in longer carrier lifetimes.

TR-PL measurements have been carried out at Instituto de Micro y Nanotecnología-CNM, (IMN-CNM-CSIC), by Dr. Benito Alén. TR-PL measurements have been performed at low-temperature exciting the samples mounted on a closed-cycle

He cryostat with a 405 nm pulsed laser light. The average excitation power density was 0.6 W/cm² at 10 MHz. Decay curves were recorded by a time-correlated single-photon counting system based on a fast-infrared photomultiplier tube attached to a 0.3-m focal length spectrometer. Time resolution obtained after the system response deconvolution is ~200 picoseconds. A multi-exponential fitting over the curves obtained from the TR-PL measurement is necessary to describe the decay dynamics across the full-time range:

$$I(t) = I(0) \sum_j A_j e^{-(t-t_0)/\tau_j} \quad (3.1)$$

Where $I(t)$ is the TR-PL signal intensity, $I(0)$ the signal intensity at the initial time, A_j are the coefficients of the exponential terms, t is the time, t_0 the time of the first adjusted point and τ_j the different decay times. Once the fitting is performed, the relative weight of each decay time (w_i) is calculated as:

$$w_i = A_i \times \frac{\tau_i}{\sum_j A_j \times \tau_j} \quad (3.2)$$

And the weighted average lifetime ($\bar{\tau}$) of the decay curve is calculated as:

$$\bar{\tau} = \sum_j \tau_j \times w_j \quad (3.3)$$

3.2.3. Photoreflectance spectroscopy

Photoreflectance (PR) spectroscopy is a modulation spectroscopic technique for the optical characterization of semiconductors materials and devices. PR is a non-destructive optical tool that can be complementary to PL.

In a PR experiment, a laser chopped at a specific frequency is used to create electron-hole pairs that periodically modulate the overall built-in electric field present in the sample. This periodic photo-perturbation of the sample induces small changes in its dielectric constants, and thus in its reflectance and transmittance, which can be detected using phase-sensitive amplifiers locked to the frequency of the pump laser. In the derivative of the modulated reflectance spectrum of the material, some prominent features (known as critical points)

appear at specific energies that are related with direct interband transitions in the electronic structure of the semiconductor.

The PR spectra can be fitted and analyzed through the third derivative functional form (TDFF) method [173]. The obtained critical point with the lowest energy is associated with the optical transition between electron and hole ground states (effective bandgap of the sample).

PR measurements have been carried out at Instituto de Energía Solar of Universidad Politécnica de Madrid, by Dr. David Fuertes Marrón. PR measurements have been performed at room temperature. A 150 W quartz-tungsten-halogen (QTH) lamp with the light going through a 1/8-m focal length spectrometer is used as the probe beam. At the same time, the sample surface is also illuminated with the 325 nm line of a 15 mW He-Cd laser (chopped at 777 Hz) that is used as the pump beam for modulating the material dielectric constant. Direct reflectance of the probe light is detected with a cooled InGaAs-photodetector. Signal is pre-amplified with lock-in techniques; finally, spectral PR signal is recorded by a computer.

3.2.4. X-ray diffraction

Interaction of X-ray with matter may happen by inelastic or elastic scattering by electrons of the atoms. In the case of elastic scattering (called Thompson scattering), the electrons oscillate like a Hertz dipole at the frequency of the incident beam and become a source of dipole radiation; the theoretical background of the XRD structural characterization technique rely on such Thompson scattering phenomenon. XRD analysis, and in particular of epitaxial films, is outlined in numerous publications [137,174,175]. XRD measurements on crystalline solids may provide information about thickness, relaxation, mismatching and crystal composition.

Some fundamental and geometrical considerations must be taken into account to understand the basics of the XRD measurements (Figure 3.9). An incident X-ray beam is scattered after impinging on the sample surface at a certain incident angle (θ) with respect to the set of equidistant crystal planes of the material, identified by the Miller indices (hkl) and separated from each other by the interplanar spacing (d_{hkl}). The scattered beam coming from the sample gives rise to maximum diffraction intensity when they produce constructive interference, which only occurs when the angle of the scattered waves with respect to crystal planes is equal to θ , and if the path difference between beams diffracted on neighboring

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planes is an integer multiple of the X-ray wavelength. Under those circumstances, the following law is fulfilled:

$$n\lambda = 2 d_{hkl} \sin\theta \quad (3.4)$$

Which is called Bragg's law. As the d_{hkl} parameter is characteristic of each crystal structure, each material has certain Bragg angles for which maximum diffraction occurs. The Bragg angle corresponding to the first order of diffraction ($n=1$) is the most characteristic one, as it provides the highest intensity reflections.

Figure 3.9: Real space illustration of the condition for Bragg diffraction.

A diagram of a typical diffractometer and their alignment axis is shown in Figure 3.10. Any XRD diffractometer has the same essential components:

- (1) An X-ray source whose emitted beam is directed to a sample stage after pass through incident beam optics.
- (2) A sample stage whose position can be accurately controlled, so wafer can be positioned as required with respect to the X-ray incident beam depending on the measurement to do. Three different motors align the sample as a whole along the x, y and z-axis and two other motors rotate the sample stage around the

z-axis (ϕ scan) and the x-axis (ψ scan) to find diffraction peaks. Finally, the goniometer mechanism moves precisely the sample stage around the y- or goniometer axis to control the X-ray incident beam angle (ω) with respect to the sample stage (ω scan).

- (3) Diffracted beam optics and a detector for the scattered intensity that can also be moved by the goniometer mechanism around the y-axis to control the detector angle (2θ) with respect to the X-ray illumination beam (2θ scan).

Figure 3.10: Diagram of an X-ray diffractometer. Three different translational axes (x, y and z) and the three possible rotational movements (ϕ , ψ and ω scans) of the sample stage are depicted, along with the detector in-plane movement (2θ scan) (adapted from ref. [175]).

The specific kind of XRD measurements performed over the samples of this Thesis are one-dimensional $\omega - 2\theta$ scans, also called rocking curves. In this kind of scans, the sample stage and the detector are rotated around the goniometer axis, and a diffracted intensity is recorded versus ω . An open detector is used to catch all the possible 2θ values so both the effects of Bragg scattering and plane rotation are combined in the measurement. A $\omega - 2\theta$ rocking configuration is useful for scanning where at least two peaks are collected (for example, a substrate peak and a layer peak). In particular, only symmetric $\omega - 2\theta$ scans have been performed, in which $\omega = \theta$, so the scan is perpendicular to the sample surface.

Thus, symmetric rocking curve are the most suitable XRD scans to collect information on epitaxial films and multi-layered structures, like SLs, grown parallel to the substrate.

The geometry in real space of this kind of measurement can be observed in Figure 3.11 a). Both ω and θ angles are equivalent, and the change in the 2θ angle must be twice the value of the change in the ω angle in each step. Since the diffraction vector is normal to the sample surface, if the grown layers are well aligned to underlying layers, at the corresponding Bragg angle of each material an intensity peak that accounts for the d_{hkl} on the layer is obtained. The angular difference between peaks on the XRD profile (Figure 3.11 b) is due to the difference in the d_{hkl} parameter of the different layers. In the case of fully strained epitaxial growth, the d_{hkl} difference is proportional to the amount of compressive or tensile strain that the epitaxially grown layer is subjected. The actual lattice parameter can be extracted knowing the d_{hkl} , and for ternary layers, the layer composition can also be extracted through Vegard's law application.

Figure 3.11: a) Illustration of symmetrical $\omega - 2\theta$ rocking curve arrangement and b) typical XRD profile obtained from this kind of scan.

Furthermore, all layers of an epitaxial structure contribute to the scattering diffractogram: different layers are the origin of different diffracted fringes, due to the different optical paths of the emitted X-rays. A periodic structure, such as a SL structure, give rise to a series of regularly distributed diffracted peaks called satellite peaks. The better the overall periodicity is, the more intense and narrower are the diffracted satellite peaks. Flatter interfaces also give rise to better satellite peaks than equivalent structures with rougher interfaces. SL thickness and periodicity can be extracted from the X-ray diffraction pattern considering separation between the satellite peaks. Details in the diffraction pattern can be further analyzed by simulation and fitting.

XRD measurements have been performed at ISOM facilities with an X'Pert Pro Pan'alytical diffractometer. The X-ray emission is provided by an X-ray tube with a Cu anode that is operated at 45 kV and 20 mA. The incident optics element counts with a parabolic X-ray mirror to focus the divergent X-ray emission to an intense monochromatic beam and with a Ge(220) asymmetrical monochromator to assure the Cu- $K\alpha_1$ (1.54056 Å) is the single emission line that illuminate the sample with high intensity. A mask of 2 mm is used to reduce the width of the X-ray beam merging the incident beam optics. The sample holder is a high precision goniometer, and the detector used is a proportional detector filled with a mix Xe/methane counting gas, the most efficient detecting Cu- $K\alpha_1$ radiation, fitted with a 1/2° anti-scatter slit. The X'Pert Epitaxy and Smoothfit software is used for simulation and fitting of the measurements.

3.2.5. Transmission electron microscopy

Transmission electron microscopy (TEM) is a very powerful tool for structural characterization. It can provide information on the internal structure of the material, so this technique can be used to study crystal structure, thickness and composition, and to observe extended defects like dislocations, grain boundaries or antiphase domains.

A TEM microscope consists of an electron gun, a sample stage and an array of electromagnetic lenses mounted inside a vacuum column. The image from electrons is projected on a fluorescent screen or on a CCD camera. Electrons are accelerated by a high potential voltage (in the range of hundreds of kVs). Such electrons are focalized using a set of condenser electromagnetic lenses, in a coherent low-angle beam that strikes the sample surface. Samples have been previously prepared to make them ultra-thin, typically less than 100 nanometres, so they become transparent to the electron beam. Some of the arriving electrons are scattered by the material atoms electrostatic potential, and some pass through the sample. In TEM there are two basic modes of operation, Bright Field (BF) and Dark

Field (DF). In DF TEM imaging mode operation, the one used during this Thesis, a set of objective electromagnetic lenses focus only scattered electrons creating an image which is after that enlarged and projected on a screen using intermediate and projector electromagnetic lenses. The darker image areas correspond to those where fewer electrons are transmitted, while the lighter image areas correspond to those where more electrons are transmitted. TEM DF imaging mode is especially sensitive to the chemical composition of samples and the presence of lattice defects.

On the other hand, the scanning TEM (STEM) operation mode has the same essential operation that TEM but in this case, the electron beam is finely focused by the condenser lenses in a spot that scans systematically across the whole sample. Electrons interact with atoms of the material for each beam position, and the diffracted intensity is registered to form a virtual image. STEM mode allows reaching atomic-scale resolution using a suitable configuration and allows performing simultaneously different TEM-related techniques such as annular DF (ADF) imaging, which can be performed at low angle (LAADF) or high angle (HAADF), or energy dispersive X-ray (EDX) or electron energy loss (EEL) spectroscopy. Both TEM and STEM operation modes are schematically represented in Figure 3.12.

Figure 3.12: TEM and STEM modes of operation in electronic microscopy.

EDX spectroscopy can be used to identify the elemental composition of materials. When high-energy electrons from the beam excite inner shell electrons of the material atoms, an empty state is created that can be filled with an electron from one of the outer shells, whose excess of energy can be released as non-radiative Auger emission or as X-rays. X-rays emitted are registered by a spectrometer. The X-rays energy emitted from a particular material is directly related to the nature of the atom where they come from. Moreover, the intensity of X-ray detected is proportional to the number of such atoms present in the sample, so the EDX technique accounts quantitatively and quantitatively for the elemental composition of the sample.

In the case of the samples of this Thesis, EDX analytical technique is suitable for obtaining Sb compositional maps and profiles with a sensitivity to Sb contents minor than 0.5% in the GaAs regions [176]. However, the characterization of the N distribution is not possible by the EDX technique as the N low atomic weight does not allow its detection. Moreover, in the quaternary $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ regions, the simultaneous presence of Sb also hinders the N characterization [177]. However, a new methodology proposed in [177,178] to detect and quantify N presence through ADF imaging has been employed on some samples of this Thesis. The scattered intensity in HAADF conditions is especially sensitive to high Z-number atoms (which is known as Z-contrast) [179]. Meanwhile, the scattered intensity in LAADF conditions is especially sensitive to a high statistic atomic displacement (SAD), which manifest itself when the atoms are displaced from its corresponding lattice sites. In the case of dilute nitride GaAs-based alloys, it is the big difference in the atomic radius of the As and N atoms which causes high enough local distortions in the material lattice to dominate the LAADF imaging contrast over the Z-contrast [180,181]. Therefore, in this kind of STEM image mode N-rich regions appears with bright contrast than the GaAs [180,181] or even the $\text{GaAs}_{1-x}\text{Sb}_x$ regions [177,182], the contrast level depending on the Sb concentration.

Specimen preparation and different types of TEM-based measurements over the samples of this Thesis have been performed by the research group of Professor David González from Departamento de Ciencias de los Materiales e IM y QI of Universidad de Cádiz. Samples in cross-sectional geometries along the [1 1 0] direction were prepared for TEM analysis by mechanical grinding and dimpling to a final thickness of 10 μm , followed by Ar^+ milling in a Gatan Precision Ion Polishing System to obtain electron-transparent specimens. TEM Dark field 002 images have been acquired in a JEOL 2100 microscopy operating at 200 kV. LAADF and HAADF imaging along with EDX spectroscopy were simultaneously performed in STEM mode in a double aberration-corrected FEI Titan3 Cubed Themis microscope operating at 200 kV. EDX mapping was carried out with four embedded Bruker

SDD detectors using ChemiSTEM technology and processed with the Bruker's ESPRIT software.

3.3. Device fabrication

Optimized bulk layers and SLs structures intended for device fabrication conform the 816 nm thick intrinsic region of p-i-n junctions grown by MBE (see Section 3.1.2). After material characterization, the final structures of interest are processed as single-junction solar cells. The processed diodes have a diameter of 200 μm and are uniformly arranged in a rectangular lattice. The typical size of the sample pieces processed is $\sim 50 \times 50$ mm; for this piece size, the number of final diodes is usually between 50 and 100 devices. All the processed diodes of each sample are tested by IV curves under dark conditions. 5-10 of them having low dark currents are selected and further analyzed under illumination conditions. Finally, 1 to 5 devices of each sample are mounted in metallic discs, and the top contact wire-bonded to a larger external contact to be able to measure them in the solar simulator setup. A sketch of the final structure of the obtained devices is shown in Figure 3.13 a).

Figure 3.13: a) Sketch of the cross-section of the processed p-i-n devices and b) top view of an actual 200- μm diameter cell with a half-moon shape top contact.

The fabrication process includes the following steps:

- (1) Cleaning of the materials surface with organic solvents (acetone and methanol) to remove any particle of dust that can worsen the adherence of the photoresist or the contacts.

- (2) After covering the top of the sample with positive photoresist resin, ultraviolet lithography, and subsequently, photoresist development is used to define the pattern of multiple 200 μm -diameter mesas on the sample surface.
- (3) A wet etching process of the defined mesa structures is performed immersing the samples in an $\text{H}_3\text{PO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ (1:1:8) acid solution. Material not covered by photoresist (material outside mesas) is etched away with an etching rate of ~ 500 nm/min. The total etching deep is set out to ~ 1.5 μm to guarantee reaching the GaAs n^+ substrate. Once the mesas are created, the remaining photoresist is lifted off using acetone.
- (4) At that point, an n-type contact consisting of Au-Ge/Au (80/200 nm) is evaporated on the bottom part of the sample forming an extended contact that is annealed at 380 °C during 30 seconds under N_2H_2 atmosphere to make it ohmic.
- (5) The sample surface is covered again with positive photoresist resin and hereafter a second ultraviolet lithography and development process are employed to define half-moon shape p-contacts on top of each mesa.
- (6) Evaporation of the p-type contact consisting of Au/Au-Zn/Au (10/80/200 nm) on top of the sample. A top view of the p-contacts is shown in Figure 3.13.b).
- (7) The next step consists in a lift-off process using acetone and assisted by an ultrasonic bath to eliminate extra p-type metal outside the contour of the top contacts defined by photolithography.
- (8) Finally, a second annealing of the metal contacts is performed at 380 °C for 30 seconds under a N_2H_2 atmosphere.

The processing of the p-i-n photodiodes is carried out at ISOM cleanroom facilities. The mask aligner machine used for the photolithography process is a Karl Suss MJB3. The positive photoresist resin used is AZ 5214E from MicroChemicals, which has a nominal thickness of 1.4 μm and is spun at 1000 rpm for 50 seconds. A chrome photolithography mask is used to define the different patterns (mesas and contacts). During the wet etching procedure, the depth of the etching is monitored using a KLA Tenkor Alpha Step IQ contact profilometer. Before starting the etching process, one of the photolithographed mesa patterns is chosen as reference. Then the stylus of the profilometer is put in contact with the sample surface and moved laterally across the mesa for a distance longer than its diameter (200 μm). In the beginning, the height of the mesa must be 1.4 μm , the nominal thickness

of the photoresist. After 60 seconds of wet etching, the same mesa is profiled again. The step increasing gives a clear idea of the etching rate.

The obtained photodevices are not optimized as solar cells. The objective of this Thesis work is to compare the solar cell efficiency of the different structures between them. First, the diodes are not covered with an anti-reflection coating (ARC), which usually reduces the refractive index contrast between the air and the semiconductor. Uncoated semiconductors reflect 30 to 40 % of the incident light, which sharply diminish J_{SC} and the PCE [183]. Moreover, high-quality solar cells can suffer severe perimeter recombination losses if their perimeter/area ratio (P/A) is high, which negatively affects their performance [184,185]. These fabricated solar cells have a P/A value of 200 cm^{-1} , so a relatively poor performance can be expected. Finally, the top contacts have not at all the optimum design. The design of the top contact in a solar cell is a fundamental issue: the area exposed to sunlight must be maximized, but the resistivity of the semiconductor surface can cause resistive series loss effects. Commercial solar cells usually use a grid structure as p-contact.

3.4. Device characterization

3.4.1. Current-voltage curves

Dark IV curves (Equation (2.1)) are a useful tool to give an idea about the quality of the fabricated photodiodes. The dark current is characteristic of each diode, and its value is directly related to carrier recombination, so it is inversely related to material quality. Moreover, the diode ideality factor is not constant for each diode but usually increases with decreasing current. Its value depends on the dominant carrier recombination mechanism. An ideality factor value close to 1 indicates an almost ideal solar cell; meanwhile, a value close to 2 indicates that solar cell is dominated by SRH recombination mechanism.

On the other hand, IV curves of the photodiodes taken under monochromatic illumination (Equation (2.2)) can be used as a first test of the photoresponse of the diodes. The analysis of how the different voltages applied during that kind of measurement affect the photogeneration and collection of the carriers can provide useful information. An increase of the photogenerated current with the applied reverse bias indicates an incomplete carrier collection [186].

IV curves at dark conditions have been systematically measured over all the fabricated diodes, and IV under monochromatic illumination have been measured in selected diodes (those with lower dark current). Both types of IV curves have been measured using a setup

located at ISOM laboratories. A schematic diagram of this setup is shown in Figure 3.14. Light emitted from a QTH lamp is dispersed through a SPEX 0.34-m focal distance grating spectrometer, filtered by a high-pass filter and after that directed to the sample stage through an optical path comprised of lenses and mirrors. The sample stage can be moved to align the photodiodes under the incident beam accurately. The samples are placed over an n-type metalized plate that allows contacting the bottom n-type contact of the sample. This plate and the top half-moon shape p-contact are contacted using micrometric probe tips. A K2401 Keithley sourceMeter which provides the bias voltage and a K6514 Keithley electrometer that measures the current are employed. The obtained spectrum is recorded using a computer.

Figure 3.14: Diagram of the IV and PC setup used in ISOM.

3.4.2. Photocurrent spectroscopy

Photocurrent (PC) spectroscopy consists in measuring the current that flows through the diode after optical absorption of photons as a function of the energy of the incident light. PC spectroscopy technique gives information about the band structure of the material. The effective bandgap of the materials can be extracted from the PC spectra calculating the

maximum of the PC derivative in the absorption edge region. Moreover, PC behavior under voltage application is used to explore the possible existence of trapping or recombination of carriers in the sample. Different voltage bias can be applied through the contacts to study carrier transport in the device: constant PC with bias indicates good carrier transport, which is preferable for solar cell operation [86]. In the case of solar cells, PC measurements are useful to clarify how the different regions or energy levels in the solar cell contribute to the PC.

The External Quantum Efficiency (EQE) of the devices can be extracted from PC measurements after a straightforward data conversion. The PC data is converted into responsivity dividing by the power per unit area of the QTH lamp (measured with a calibrated Si photodiode) multiplied by the diode top metal-free area, and lately, responsivity is converted into EQE multiplying by photon energy divided by the electron charge. The EQE depends on the absorption of light and the collection of charges and is defined as the ratio of the number of charge carriers collected by the solar cell to the number of incident photons and is commonly used for solar cell characterization, as it accounts for the energy conversion efficiency of the cell.

$$EQE = \frac{\text{current}/q}{\text{total power of photons}/h\nu} \quad (3.5)$$

PC have been measured in the same diodes where IV curves under monochromatic illumination have been taken. PC measurements have been carried out in the same setup located at ISOM facilities in the same setup used to take dark and monochromatic IV curves shown in Figure 3.14.

3.4.3. Current-voltage curves under AM1.5G solar spectrum

Standard solar cell characterization under standard AM1.5G spectra (Figure 2.1) of the solar cells of this Thesis has been conducted at Instituto de Energía Solar (IES) of Universidad Politécnica de Madrid, with the help of Dr. David Fuertes and Prof. Carlos del Cañizo. The setup employed is an Oriel solar simulator with sample temperature control at 25 °C. This setup is not intended for measuring micro- solar cell, so previous mounting of the samples and wire-bonding of the top contacts of a few devices is required (see Section 3.3.). The standard solar cell measurement allows comparing the characteristic parameters (V_{OC} , J_{SC} , FF , PCE and W_{OC} , described in Section 2.1.3) of the solar cells of this Thesis among them and with any other value reported in the literature.

3.5. Rapid thermal annealing

Rapid thermal annealing (RTA) is a process consisting in heating rapidly a material up to high temperatures (usually between 300 and 1200 °C). Once the soaking temperature is reached, it is held for a short time (typically a few seconds) and then it is cooled back fast [187].

This high-temperature heating treatment provides enough energy to the crystal materials to promote homogenization in their atomic arrangement: it helps, for example, to place dopant atoms on substitutional lattice sites and to reduce crystal defects. The short time of the treatment avoids large-scale redistribution of dopants within the semiconductor, which is especially important in p-n junctions designed for solar cell purposes.

RTA process is commonly used to improve material quality and optical properties of semiconductor materials, including dilute nitrides (see Section below). In our case, besides the structural design and growth-based strategies, a post-growth RTA treatment could further improve the structural, optical and electrical properties of the GaAs(Sb)(N) structures. For this reason, RTA cycles have been performed over some pieces of different GaAs(Sb)(N) samples (SLs structures as well as bulk layers), that are characterized through PL and XRD measurements before and after the annealing process. Different annealing temperatures (between 750–850 °C) have been used to determine the optimum one for each structure; the annealing time is set up at 30 seconds. The optimum temperature is determined through PL analysis, and afterward, a new piece of each structure is annealed at such temperature, and a whole device processing is carried out, followed by device characterization. The performance of the RTA solar cells is compared to that of the as-grown ones.

RTA process have been performed at ISOM. The RTA system is an Ulvac MILA-3000 furnace, which provides fast heating through a source of infrared radiation. The samples are annealed in a N₂ inert atmosphere, and the temperature is controlled by a thermocouple contacted to the sample stage. The pieces of samples are encapsulated between two GaAs-wafers to minimize As desorption during annealing.

3.5.1. Effect of rapid thermal annealing on dilute nitride materials

As mentioned above, an adequate RTA process can improve luminescence of dilute nitrides alloys: typically, the II of the band-to-band PL peak increases and the FWHM decreases, which has been observed in Ga_{1-x}In_xAs_{1-y}N_y, [188–191], GaAs_{1-y}N_y [155,192]

and $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ [193–195]. RTA processes have been already applied to dilute nitrides conceived for photovoltaic uses with the aim of improving the solar cell performance [56,72,81,196,197]. The improvement in the material properties upon annealing has been usually attributed to a reduction of N-related point defects acting as non-radiative recombination centers [93,155,188,192,193], and/or to an improvement of the alloy homogeneity [190,193].

Also, annealing process typically provokes blueshift of the band-to-band PL peak in dilute nitrides. Several different mechanisms have been proposed as the cause of this usually undesired effect. It has been attributed to changes in the alloy composition homogeneity, due to effects such as Ga/In intermixing, out-diffusion of N atoms [154,198–200] or As/Sb interdiffusion [201]; it also has been attributed to a reduction of the band tailing non-recombination centers [92,193,202]. However, according to the most widely accepted interpretation, the blueshift in dilute nitride alloys arises from a short-range order material reorganization after annealing, without any modification of the element contents of the alloy [84,189,203,204].

This concept has been theoretically modeled for $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ [205] and suggested for $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ [92,195]; it has been experimentally demonstrated for both $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ [206,207] and $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ [195]. The explanation is based on the behavior of the N-bonds upon annealing: In $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$, the thermal energy provided modifies the short-range order of the alloy, changing the preferential bond configuration from the GaN+InAs metastable one obtained during the growth of the alloy to the equilibrium GaAs+InN configuration, which is the one of minimum strain. This modification in the atomic configuration is predicted to reduce the bandgap bowing in $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$, increasing the bandgap energy without variations in the element concentration, which would be the origin of the blueshift. In the case of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$, the annealing process is also expected to provoke short-range atomic rearrangements which would minimize the local strain around the N or Sb lattice sites. However, in the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ alloy, N atoms can only be bonded to Ga atoms; therefore, the influence of the V-group As or Sb atoms around the N atoms is only of second-neighborhood atomic order. For this reason, smaller blueshift can be expected in $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ than in $\text{Ga}_{1-x}\text{In}_x\text{As}_{1-y}\text{N}_y$ [195].

4. Strain-balanced GaAs(Sb)(N) structures: growth and material properties

4.1. Introduction

As described in Chapters 1 and 2, MJSCs made by assembling semiconductor materials with different bandgap energies have held the record conversion efficiencies for many years and are currently approaching 50 %. The theoretical SQ limit is used to design optimum multi-junction designs with the right bandgap energy combination to reach the maximum energy conversion efficiency. It has been established that a 1.0–1.15 eV material lattice-matched to GaAs/Ge is required to conform to one of the multi-junction sub-cells with the optimum structure. Nevertheless, the lack of suitable, easy-to-control semiconductor materials is hindering the achievement of the predicted efficiencies, since the only possible candidate materials were up to now complex quaternary and quinary dilute nitride alloys with inherent material quality problems that degrade carrier dynamics.

The strain-balanced GaAs(Sb)(N)-based SLs with type-II band alignment are proposed as suitable candidates to form this relevant sub-cell. The advantages of using $\text{GaAs}_{1-x}\text{Sb}_x\text{N}_y$ over others dilute nitride materials, along with the additional advantages over the bulk that result from the type-II band alignment in SLs, have already been extensively addressed in Chapter 2.

In this Chapter, the structural and optical properties of bulk, type-I and type-II SLs with small N and Sb contents (those needed to reach ~ 1.20 eV bandgap) are studied and compared. Then, a series of type-II SL samples with different period thickness are structurally and optically characterized. The interplay between carrier lifetime, electronic coupling and extraction efficiency in this type-II SLs is analyzed experimentally and theoretically, as well as the critical role of the period thickness. As far as we know, there is almost no literature on these structures. A four period type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ MQW structure without strain balance has been already grown by Metalorganic Vapor Phase Epitaxy (MOVPE) on a GaAs substrate [208] for laser applications. Nevertheless, to the best of our knowledge, different type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ strain-balanced SL

structures with elevated number of periods have been grown by MBE and systematically analyzed for the first time during this Thesis. This Chapter is based on results presented in articles [182,209–211] with permission of the corresponding journals.

The general description of the growth process of the samples studied in this Chapter can be found in Chapter 3, Section 3.1.2. As already mentioned there, before the growth of the samples presented in this Chapter growth and careful analysis of different $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-y}\text{N}_y$ layers were performed in order to calibrate the Sb and N contents effectively introduced in ternary structures as a function of the beam fluxes and the growth rate employed, which are defined as nominal contents thorough this Thesis. This growth calibration can be found in Appendix A. The growth details of the active region of all the samples are summarized in Table B.1 in Appendix B. The description of every set of samples is at the beginning of each corresponding Section in this Chapter.

4.2. Results and discussion

4.2.1. Bulk versus superlattices: material properties

In the first series of samples, four different SLs and one bulk structure are compared. The SLs are formed by 18 periods with a constant nominal period thickness of 12 nm (6 nm+6 nm) consisting of: $\text{GaAs}/\text{GaAs}_{1-y}\text{N}_y$ (sample *SL-N*), $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}$ (sample *SL-Sb*), $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$ (sample *SL-I* with expected type-I band alignment) and $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ (sample *SL-II* with expected type-II band alignment). The fifth sample consists of a 200 nm thick $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ bulk layer (sample *bulk*). A scheme of the epitaxial structure and the expected band structure of all samples is shown in Figure 4.1 a) -e). A sketch of the maximum of the distribution probability of electron and hole wavefunctions are represented in the Figure in blue and red, respectively. All the samples were grown under the same Sb and N nominal fluxes (corresponding to ~1.2 % and ~3.25 % nominal N and Sb contents, respectively), whose combination gives rise to a ~1.2 eV bandgap. The calibration of the N and Sb fluxes in the ternary compounds is shown in Appendix A. Therefore, only half the amount of N and Sb was nominally used to fabricate the SL structures as compared to the bulk, and the amount of low bandgap active material was half in these structures. The description of the active layers of each of these samples is in Table B.1, Appendix B.

4.2.1.1. Compositional control and material quality

All samples were structurally analyzed by TEM. DF 002 representative images of all of them are shown in Figure 4.1 f) -j). In this chemically sensitive TEM imaging mode, Sb-rich regions appear brighter whereas N-rich regions appear darker than GaAs regions. It can be observed that all SLs structures exhibit flat interfaces and there is no evidence of dislocations or any other sort of extended defects and that the periodicity is regular throughout the whole structure. A detailed analysis demonstrates that the four SLs and the bulk structure are also completely pseudomorphic. Focusing on samples *SL-I* and *SL-II*, their estimated period thicknesses are 12.7 nm and 12.9 nm respectively, slightly larger than the nominal value of 12 nm due to a minor increase in the growth rate. Also, in the DF 002 images, the interface contrast appears more abrupt in *SL-II* than in *SL-I*, probably indicative of reduced Sb segregation [212].

Figure 4.1: Sketch of the epitaxial layout and band alignment (not to scale) of the active region of the samples a) *SL-N*, b) *SL-Sb*, c) *SL-I*, d) *SL-II* and e) *bulk*. DF 002 TEM images of samples f) *SL-N*, g) *SL-Sb*, h) *SL-I*, i) *SL-II* and j) *bulk*.

The samples were also investigated by XRD. Figure 4.2 a) -b) shows the $\omega - 2\theta$ scans around the (004) GaAs Bragg reflection of the *SL-N* and *SL-Sb* samples, respectively, along with the simulation that best-fit the experimental scans. Both SL pattern shows the 33.0239° peak corresponding to GaAs, a main layer peak that quantify the composition of the ternary

layer and a series of evenly spaced peaks arising from the SL periodicity, the satellite peaks. The addition of N on the GaAs matrix causes tensile strain (layer peak located at higher angles than the GaAs one); on the other hand, the addition of Sb causes compressive strain (layer peak at smaller angles than the GaAs one).

Figure 4.2: a) $\omega - 2\theta$ scan (bright line) and the fitted simulation (faded line) of the SL-N sample, b) $\omega - 2\theta$ scan (bright line) and the fitted simulation (faded line) of the SL-Sb sample and c) $\omega - 2\theta$ scans of samples SL-N and SL-Sb (below) and of the samples SL-I, SL-II, and bulk (above).

The simulations determine good agreement of the different layers (active and capping) nominal thickness to the real values. Also, assuming from TEM analysis that structures are pseudomorphic, the N and Sb compositions are estimated to be 1.20 % and 3.25 % in their nominal layers, respectively. These two content values fulfill the lattice matching condition for $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ on GaAs, as it is qualitatively evidenced by the symmetrical position of the main layer peaks to the substrate peak in both spectra, which is easily observed in Figure 4.2 c). Moreover, in the SL-N diffractogram, the intensity of all the simulated peaks fit the real ones; meanwhile, in the SL-Sb, simulated satellite peaks are more intense than in the real scan. This satellite peaks behavior points to that the SL-Sb structure has reduced quality interfaces, likely due to Sb segregation.

Assuming that there is no Sb-N interaction during growth that could modify the composition, lattice matching is expected in the rest of the samples, grown with the same N and Sb fluxes. Figure 4.2 c) shows the $\omega - 2\theta$ scans around the (004) GaAs Bragg reflection of the SL-I, SL-II and bulk samples. In the SL-I and bulk XRD profiles, the main

peak appears shifted towards the tensile region of the XRD diffractogram. These siftings indicate that the *SL-I* and *bulk* compositions are not equivalent to the ternaries ones, due to the concomitant presence of N and Sb in the growth front. This effect is particularly strong in the bulk sample, where a more significant shift from the GaAs peak appears. The presence of both elements affects the incorporation of each other, and this effect depends on the amount of N and Sb present, which makes an accurate composition control very difficult. However, the alternate introduction of Sb and N atoms in the growth surface to growth a type-II SL sample effectively avoids the interaction between both species during growth. The perfectly lattice-matching of the *SL-II* diffractogram indicates that composition is accurately adjusted so the expected contents were incorporated and the overall strain precisely compensated. Moreover, the narrower main peak in the SLs as compared to the bulk structure could be indicative of a better strain and material quality [174], which would mean clustering reduction in the SL structures. Remarkably, the satellite peaks are also narrower and more intense in *SL-II* as compared to *SL-I*, reflecting the higher interface quality when Sb and N are incorporated separately, in agreement with what was observed by TEM.

In the SLs nominal design, Sb and N atoms are considered to be perfectly kept in their corresponding layers, giving rise to a perfectly regular staggered bandgap structure, as sketched in Figure 4.1. However, the Sb trend to segregate [213–215] during epitaxial growth because of the preferential incorporation of As over Sb in the GaAs matrix seems to be affecting the Sb-containing SLs according to DF TEM images. On the other hand, N segregation does not usually happen if the samples are grown at relatively low-temperature [216], like is the case of these samples. The DF 002 images of *SL-N* and *SL-Sb*, in Figure 4.1 f) and g), respectively, can be used to study the possible existence of Sb segregation assuming both ternary samples were measured under the same TEM conditions. Due to the different image contrast caused by N and Sb, a qualitative estimation of the N and Sb presence along the layers can be extracted for each ternary SL analyzing the scattered intensity at different points of the alloy normalized to the pure GaAs scattered intensity.

Figure 4.3 shows normalized-to-GaAs scattered intensity profiles along the growth direction for the first layers of samples *SL-N* and *SL-Sb*. Color lines represent a semi-quantitative estimation of the respective N and Sb contents. In sample *SL-N* (Figure 4.3 a) the profile has a stepped shape, meaning N segregation to GaAs layers does not exist, as expected. On the other hand, in sample *SL-Sb* (Figure 4.3 b) segregation keeps Sb from remaining contained spatially into $\text{GaAs}_{1-x}\text{Sb}_x$ nominal regions, but it spreads into the nominally Sb-free regions: the Sb content profile in sample *SL-Sb* shows a spiky shape because of the segregation. The Sb content is slowly incorporated at first and increased until

reaching a maximum during the time the Sb shutter is open, and then slowly decay when the Sb flux is interrupted. The Sb content in the GaAs layer does not decay to zero at any point; when the Sb flux impinges again in the sample surface, there is already remaining Sb on the growth surface. Then, the initial growth conditions at the beginning of second and further $\text{GaAs}_{1-x}\text{Sb}_x$ layers are different from those in the first deposited layer. For this reason, the Sb content in the first layer is smaller than the others.

Figure 4.3: Estimated N and Sb content (left axis) and normalized scattered intensity (right axis) along the growth direction in the first periods of the a) SL-N and b) SL-Sb samples.

About SLs with the presence of both N and Sb atoms, the reduced Sb segregation in *SL-II* sample as compared to *SL-I* sample is confirmed through Sb mapping performed by EDX measurements. Different regions of the two SLs samples were analyzed, and all of them give similar results; Figure 4.4 shows a representative Sb map of each SL.

Figure 4.4: EDX maps of the Sb distribution in SL-I and SL-II samples along the growth direction.

A stronger Sb segregation into nominal Sb-free layers is observed in *SL-I*. Moreover, the Sb distribution is less uniform in *SL-I*, with the existence of more and bigger Sb-rich regions (with Sb content up to ~6 %). The spatial separation of N and Sb in the type-II structures also results in a more homogeneous distribution of Sb within the Sb-containing layers.

4.2.1.2. Effective bandgap energy and carrier lifetime

The higher control over composition achievable with the type-II SL as compared to the type-I SL or the bulk is an essential feature for energy tuning of the bandgap in MJSC applications. The energy of the PL emission peak can be taken as the bandgap energies of the samples (see Section 3.2.1). Figure 4.5 shows PL spectra measured in the samples at 15 K.

Figure 4.5: 15 K PL spectra of samples *SL-N*, *SL-Sb*, *SL-I*, *SL-II* and bulk. The indicated energies in meV represent the energy shift of the PL peak energy of each sample with respect to the GaAs bandgap (1.46 eV).

The energy shift of the *SL-II* emission peak with respect to the bandgap of GaAs (dashed vertical line) is 280 meV. This energy shift fits almost perfectly with the combined energy shifts observed for the ternary samples *SL-Sb* (27 meV) and *SL-N* (250 meV). This is a unique property of this system: independent tuning of the VB and CB, and thus of the bandgap energy, can be achieved by independently controlling the Sb and N concentrations. The bandgap energy control is hard to reproduce in the bulk quaternary alloy. All samples were fabricated using the same nominal concentrations and, yet, the sample *bulk*

significantly redshifts from the nominal bandgap value. Finite differences calculations (described in Appendix C and shown in Section 4.2.2.2) suggest that the quantum confinement effect in an equivalent 12 nm period type-II SL structure is only ~ 39 meV, which would only partially explain the PL peak difference of 55 meV as compared to the bulk. The redshift of the PL peak energy and the tensile position of the XRD central peak shown in Figure 4.2 c) instead points to an unwanted excess incorporation of N in this sample (and, to a lesser extent, also in the *SL-I* sample). This effect was suppressed in the *SL-II* sample using alternate deposition of the ternary compounds. The tails observed at low energies of the PL peaks could be related with the existence of deep defects within the bandgap, or the presence of compositional inhomogeneities (See Section 3.2.1.1).

TR-PL decay curves measured at the PL peak energy provide information about the carrier lifetime within each sample. As shown in Figure 4.6, *SL-I* and *bulk* samples have similar decay dynamics, clearly different from those of sample *SL-II*. A multi-exponential fitting is necessary to describe the decay dynamics across the full-time range. The carrier lifetimes (τ) in nanoseconds and their relative weights (w) along with the weighted average of the characteristic times in the different decay regimes ($\bar{\tau}$) are shown in Table 4.1.

Figure 4.6: TR-PL decay curves measured at the PL peak energy of the samples *SL-I*, *SL-II* and *bulk*. The deconvoluted decay times are in Table 4.1.

The more considerable differences occur for long times after the excitation, where the decay of the luminescence of sample *SL-II* becomes three times slower (decay constant changes from ~ 15 to ~ 49 ns). The existence of this significantly longer radiative lifetimes at the PL peak energy for sample *SL-II* strongly supports the predominance of type-II band

alignment and recombination, which is additionally supported by the calculated $SL-I/SL-II$ ratio between the electron-hole wave function's overlap (inversely proportional to the radiative lifetime), which is ~ 3 (see Section 4.2.1.2). The slower carrier recombination could lead to an enhanced carrier extraction and, therefore, an improved PC [217]. Remarkably, in this sample, not only the PL band is narrower, but the integrated PL emission is the most intense despite the longer carrier lifetime (see Figure 4.5). The improved PL peak is a clear indication of the improved crystal and interface quality produced by type-II SL, also underlined by the fact that the PL of bulk GaAs_{1-x-y}Sb_xN_y layer is much weaker despite having twice as much active material.

	τ_1 (ns) / w_1 (%)	τ_2 (ns) / w_2 (%)	τ_3 (ns) / w_3 (%)	$\bar{\tau}$ (ns)
<i>bulk</i>	---	15.1 / 76.2	2.9 / 23.8	12.2
<i>SL-I</i>	---	15.5 / 78.0	3.3 / 22.0	12.8
<i>SL-II</i>	49.1 / 24.6	17.0 / 54.7	4.2 / 20.7	22.2

Table 4.1: Carrier lifetimes with their corresponding relative weights, and weighted average carrier lifetimes of samples *bulk*, *SL-I* and *SL-II*, obtained from the TR-PL measurements.

4.2.2. Type-II superlattices

To further investigate the promising properties of the type-II SL structures, a set of samples consisting of type-II SLs with different nominal period thicknesses of 3, 6, 12, and 20 nm (SL_3 , SL_6 , SL_{12} , and SL_{20} samples, respectively) are grown and studied. All of them have a total thickness of 200 nm and the same Sb and N nominal fluxes than the previous series of samples. Table B.1 in Appendix C shows the growth details of the active layers of this set of samples.

4.2.2.1. Periodicity, material quality and segregation

XRD $\omega - 2\theta$ scans around the (004) GaAs Bragg reflection are shown in Figure 4.7. The close match of the main SL reflection peak with the GaAs Bragg angle in all the samples indicates an accurate composition and lattice-matching control within the whole range of periodicity. Spacing between subsequent satellite peaks allows for a precise estimation of

the period thickness, found to be 3.1 nm, 6.4 nm, 12.6 nm and 19.1 nm respectively, close to the nominal design values.

Figure 4.7: $\omega - 2\theta$ scans performed on samples SL_3 , SL_6 , SL_{12} and SL_{20} .

DF 002 TEM representative images of all the samples are shown in Figure 4.8. Sb-rich regions appear brighter whereas N-rich regions appear darker than GaAs regions.

Figure 4.8: DF 002 TEM images of samples a) SL_{20} , b) SL_{12} , c) SL_6 and d) SL_3 .

A detailed analysis demonstrates that the SLs are completely pseudomorphic, with no evidence of plastic relaxation through dislocations or any other sort of extended defects. All samples show relative abrupt interfaces and a homogeneous composition along the whole

structure. As shown before, both interface roughness and alloy inhomogeneity are reduced in these structures compared to the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$ type-I SL counterparts [218]. The periodicity is also regular throughout the whole structure with estimated period thicknesses of 2.7, 6.7, 13.2 and 19.4 nm for SL_3 , SL_6 , SL_{12} , and SL_{20} , respectively, in good agreement with the nominal and XRD values. Both XRD and TEM indicate a good composition and periodicity control even for thin periods in the range of 3 nm.

The method used to estimate Sb and N contents in ternary SLs presented in Section 4.2.1.1 cannot be applied in DF images of samples with the presence of both kinds of atoms as in $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs. A behavior similar to that observed in $SL\text{-N}$ and $SL\text{-Sb}$ samples can be expected in these SLs: N confinement in the corresponding layers and Sb segregation. EDX maps are used to perform a quantitative study of the Sb content and segregation in samples SL_{20} , SL_{12} and SL_6 . EDX Sb maps taken at different areas provide similar Sb content profiles, indicating a high growth homogeneity. Averaged line Sb profiles extracted from EDX maps along the growth direction of the three different SL samples are shown in Figure 4.9. Sb content profiles simulated through an Sb segregation model (explained in appendix C) are also shown.

Figure 4.9: Experimental (black squares) and simulated (red lines) Sb profiles along the growth direction for samples a) SL_{20} b) SL_{12} and c) SL_6 .

Each profile shown is taken for a different number of periods located at different positions of the SL structures: in SL_{20} and SL_{12} , profiles are taken in the last grown periods but in SL_6 profile is taken in the first grown periods. In SL_{20} and SL_{12} Sb content profiles are similar in the different periods shown. However, the Sb profile in sample SL_6 shows that Sb has lower incorporation in the very first grown layers, because the absence of previously segregated Sb in the first growth front, as explained earlier for $GaAs_{1-x}Sb_x/GaAs$ SLs. Indeed, in type-II SLs Sb incorporation profiles have the same asymmetrical behavior than in the ternary $SL-Sb$ (Figure 4.3. b). There is a slow incorporation of Sb in the nominal $GaAs_{1-x}Sb$ layer, and a subsequent gradual Sb decay in the nominal $GaAs_{1-y}N_y$ layer. The Sb maximum appears just at the interface between the $GaAs_{1-x}Sb_x/GaAs_{1-y}N_y$ layers; meanwhile, the Sb minimum occurs at the $GaAs_{1-y}N_y/GaAs_{1-x}Sb_x$ interface, though it decreases when the period thickness increases ($\sim 1.0\%$ for SL_6 , $\sim 0.7\%$ for SL_{12} and $\sim 0.4\%$ for SL_{20}). As the thickness of the $GaAs_{1-y}N_y$ layer increases, the amount of accumulated Sb that reaches the $GaAs_{1-y}N_y/GaAs_{1-x}Sb_x$ interface before the next $GaAs_{1-x}Sb_x$ layer growth decreases.

Therefore, because of the Sb segregation in the nominal $GaAs_{1-y}N_y$ layers, the type-II SLs have an actual profile consisting of $GaAs_{1-x}Sb_x/GaAs_{1-x-y}Sb_xN_y$ alternating layers instead of the nominal $GaAs_{1-x}Sb_x/GaAs_{1-y}N_y$ ones. When the period thickness of the SL increases, the amount of Sb segregated in the $GaAs_{1-y}N_y$ layer is reduced, and the structure becomes more similar to the nominal design. This variation in the SL structure leads to a modified SL electronic band structure, which is, in principle, an undesired phenomenon. Different strategies based on shutter operation can be used to avoid deviation during growth from the nominal SL design, which are described in the Future work Chapter, Section 8.1.1.

4.2.2.2. Quantum confinement and miniband formation

PL measurements at 15 K were carried out to evaluate the impact of the SL period on the optical properties. As shown in Figure 4.10 a), an increasing SL period thickness results in a blueshift of the PL peak. Indeed, the effective bandgap energy in $GaAs_{1-x}Sb_x/GaAs_{1-y}N_y$ SLs achievable by reducing the period thickness should tend to that of a randomly alloyed bulk structure containing the same overall amount of Sb and N [131]. The PL redshift with the period thickness is accompanied by a narrowing of the FWHM, from 26 meV in SL_{20} to 104 meV in SL_3 , and an enhancement of the II by a factor of ~ 1.6 from SL_{20} to SL_3 (inset of Figure 4.10).

Figure 4.10: a) 15 K PL spectra of samples SL₂₀, SL₁₂, SL₆ and SL₃. The inset shows the II (left axis) and the FWHM (right axis) of the spectra as a function of the period thickness. b) Room temperature spectra (black dots) and TDFF fitting (red lines) of the same SL structures.

PR measurements (Figure 4.10 b) have been carried out to get insight into the tuning of the effective bandgap energies with period also at room temperature. The PR spectra have been analyzed through the TDFF method [173]. The obtained critical point with the lowest energy is associated with the optical transition between electron and hole ground states: the energy of such first critical point energy is reduced when the period thickness of the SL increases.

Both PL and PR measurements indicate that the period thickness of type-II SL structures is an additional parameter, besides the Sb and N contents, that allows the tunability of the effective bandgap in relevant spectral regions, while the structure keeps lattice-matching condition.

Electronic band structure simulations through finite differences method (described in Appendix C) are performed to make also a theoretical calculation of the effective bandgap tunability through the SL period thickness. The simulations consider the whole 18 period GaAs_{1-x}Sb_x/GaAs_{1-y}N_y SL structures with the period thickness and the Sb and N contents (3.25 % and 1.2 %) that have been estimated by XRD. To illustrate the obtained results, Figure 4.11 a) shows the potential profiles of one GaAs_{1-x}Sb_x/GaAs_{1-y}N_y period for each of the four SL structures, with the calculated confined states depicted inside the well.

Figure 4.11: a) Confined energy levels calculated taking into account the whole SL structures SL_3 , SL_6 , SL_{12} and SL_{20} are displayed in a single period of each SL. b) Comparison between the measured PL peak energy (black dots), the PR critical point with the lowest energy (red triangles) and the calculated ground transition energies (blue squares) for each SL structure.

Simulations reveal an increasing evidence of miniband formation by reducing the period thickness with respect to SL_{20} , whose relatively thick period gives rise to standard quantum well-like confined states. For thinner periods, the stronger interaction among closer confined states yields stronger wavefunction overlap, broadening of minibands and increased density of states in both CB and VB [157]. Therefore, the evolution of the PL peak FWHM and II in PL spectra as a function of period thickness is governed by the progressive formation of minibands. The reduced period thickness induces a larger confinement energy of the ground state, leading to a blueshift of the effective bandgap, following a similar trend as that observed in the PL peak energy and the PR critical point with the lowest energy.

The effective bandgap energies for each SL extracted from simulations, along with the values extracted from PL and PR measurements, are represented in Figure 4.11 b). The effective bandgap energy increases rapidly as the SL period decreases in all cases. A bandgap tunability of ~ 70 – 100 meV is achieved within the investigated range. These findings confirm the presence of quantum confinement in the structures and therefore, the ability to tune the effective bandgap by varying the period thickness of the SL. Bandgap energies extracted from 15 K PL measurements show a different trend than values obtained from PR measurements or band structure simulations. When the period thickness is reduced, the PL values are close to the PR values. This reduction in the expected bandgap energy for

smaller periods that arises at low-temperature can be due to a carrier localization effect appearing for low period thickness. For these smallest periods, there is a stronger interaction between N and Sb due to the segregation of the latter, which could lead to a higher density of clusters in the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ layers, as was the case in the type-I SLs (see Figure 4.4).

4.2.2.3. Radiative lifetime tuning

The thickness period determines the electronic coupling in the structure, which should also affect the radiative lifetime. Figure 4.12 a) shows TR-PL decay curves at the PL peak maxima from this set of SL structures, together with the *bulk* sample from the previous series. The change in the decay dynamics follows a clear trend whereby thinner period thickness leads to faster PL extinction, the decay behavior progressively approaching that of the bulk material.

Figure 4.12: a) TR-PL decay curves measured at the PL peak energy of samples SL₃, SL₆, SL₁₂, SL₂₀ and bulk. The deconvoluted decay times are in Table 4.2. b) $\bar{\tau}$ values of the different type-II SLs (red circles) and the calculated inverse of the electron-hole wavefunction overlap for type-II (red stars) and type-I (blue stars) SLs as a function of period thickness. The $\bar{\tau}$ values of the SL-I sample (blue circle) and the bulk sample (dotted line) are also shown.

A multi-exponential fit was carried out to describe the different regimes in the decay dynamics along the full range of time and quantitatively compare the recombination nature in the different structures. The carrier radiative lifetimes (τ) estimated from the different decay regimes with their relative weights (w), as well as the weighted average of the characteristic times in the different decay regimes ($\bar{\tau}$) are shown in Table 4.2; the

characteristic times of the *bulk* sample are shown in Table 4.1. Significantly weaker wavefunction overlap for period thickness starting from 12 nm yields the appearance of a long characteristic time as a consequence of a more pronounced type-II-like nature.

In a first approximation, the carrier radiative lifetimes can be approximated by the $\bar{\tau}$ values, which are represented in Figure 4.12 b) together with the inverse of the calculated electron-hole wavefunction overlap (calculations described in Appendix C), values directly proportional to the radiative lifetimes. Such calculations as a function of the period thickness were also carried out for GaAs_{1-x-y}Sb_xN_y/GaAs type-I SLs with the same Sb and N contents for comparison, and the lifetimes for a 12 nm period type-I SL (sample *SL-I* from the previous series) were experimentally measured (see Table 4.1). As observed, there is evident good agreement between the tendencies for experimental radiative lifetimes and the theoretically estimated values for the inverse of the wavefunction overlap. A substantial reduction of carrier lifetime for thinner periods is observed and predicted for the type-II SLs, which tends towards that of the bulk structure for periods below 6 nm. Nevertheless, the inverse of the wavefunction overlap hardly varies with period thickness for type-I SLs, with a value close to that of the bulk structure. Therefore, carrier radiative lifetime can be widely tuned by modifying the electronic coupling through the period thickness in type-II SLs, something which is not achievable in type-I SL counterparts. Long carrier lifetimes of ~50 nanoseconds can be achieved for thick periods in spite of the relatively small potential barriers due to the “low” N and Sb contents in these SLs. Moreover, carrier lifetimes characteristic of bulk and type-I SLs are achievable from a type-II SL structure with sufficiently reduced period thickness.

	τ_1 (ns) / w_1 (%)	τ_2 (ns) / w_2 (%)	τ_3 (ns) / w_3 (%)	$\bar{\tau}$ (ns)
<i>SL</i> ₂₀	54.9 / 55.0	16.2 / 37.0	3.0 / 8.0	36.4
<i>SL</i> ₁₂	49.1 / 24.6	17.0 / 54.7	4.2 / 20.7	22.2
<i>SL</i> ₆	---	16.7 / 84.9	4.1 / 15.1	14.8
<i>SL</i> ₃	---	15.3 / 82.4	3.0 / 17.6	13.1

Table 4.2: Carrier lifetimes with their corresponding relative weights, and weighted average carrier lifetimes of samples *SL*₃, *SL*₆, *SL*₁₂ and *SL*₂₀ obtained from TR-PL measurements.

4.2.2.4. Extraction efficiency

The change in electronic coupling caused by the SL period thickness variation must have a critical impact on carrier transport and extraction efficiency of the structures when operating as solar cells. Quantum kinetic calculations based on the non-equilibrium Green's function formalism (NEGF) have been performed to simulate photocarrier extraction on type-II SLs with a 1.2 eV bandgap and three different period thickness, 12, 6 and 3 nm, working as photovoltaic devices. A brief description of the method is in Appendix C. The simulations consider a whole p-i-n SL structure (with an active layer thickness of 800 nm) which correspond to a built-in field of 15 kV/cm without any voltage bias applied. Elastic scattering, as well as inelastic scattering of electrons and holes with optical phonons, are considered in the simulations. Figure 4.13 shows the calculated electron and hole one-dimensional local density of states for these SLs.

Figure 4.13: Simulations of the local density of states (for $k_{\parallel}=0$) of 1.2 eV type-II SLs with 3, 6 and 12 nm period thickness (taken from ref. [211]).

For the 3 nm period SL, both electrons and holes are delocalized along the periods. For the 6 nm period SL, the hole states are confined into a specific well, but the electron wave functions are still delocalized. Finally, for the 12 nm period SL, both electron and hole ground states are fully localized inside single wells.

Simulation of transport mechanism in SLs is performed through calculations of spectral PC density after above-bandgap monochromatic illumination. Figure 4.14 shows simulated spectra for the same SL structures under 1.25 eV illumination.

Figure 4.14: Simulations of the spectral current density under 1.25 eV monochromatic illumination of 1.2 eV type-II SLs with 3, 6 and 12 nm period thickness (taken from ref [211]).

The different types of carrier localization as a function of the period thickness have an impact on the transport regime of the SLs (see Section 2.3.2). For the 3 nm period SL, transport proceeds through the miniband and photocarrier extraction is quasi-ballistic for both electrons and holes. For the 6 nm period SL, electron extraction is still quasi-ballistic, while the transport of holes by tunneling is no longer so fast, which leads to the appearance of a hot carrier current component that is thermally activated by the absorption of optical phonons. Finally, for the 12 nm period SL, not only holes but also electron transport has developed a significant thermal scape component and the tunneling proceeds in a sequential fashion with pronounced inter-period carrier relaxation. The predicted change in the transport behavior from quasi-ballistic extraction to sequential resonant tunneling combined with thermionic scape transport leads to a reduction in the photocarrier extraction efficiency with the period thickness.

Figure 4.15 shows the calculated carrier extraction efficiency for different kinds of SLs as a function of their period thickness. For type-II SLs with a bandgap energy of 1.2 eV, extraction efficiency is 100 % for a 6 nm period and significantly decreases for periods above 8 nm: there is an extraction efficiency of ~90 % for a 10 nm period, which is reduced to ~75 % for a 12 nm period SL and decays further for longer periods. Nevertheless, this predicted degradation of the extraction efficiency in type-II SLs is much slower than in equivalent type-I SLs, where it is already reduced to ~40 % for a 10 nm period; this is due to the longer radiative lifetimes and reduced radiative recombination inside the wells attributable to the type-II band alignment, which improve carrier extraction efficiency. The

type-II SLs allow a broader range of period thicknesses to be implemented in the design of devices with a reasonable extraction efficiency; this is an additional advantage of the type-II structures.

Figure 4.15: Calculated carrier extraction efficiency as a function of the period thickness for 1.2 eV type-II (black dots) and type-I (black circles) SLs, and for 1.0 eV type-II SLs (red dots).

NEGF simulations have also been performed, with the same simulation conditions, on type-II SLs with larger N and Sb contents to get a reduced 1.0 eV bandgap and an active layer thickness of 800 nm. The calculated carrier extraction efficiency is also shown in Figure 4.15. The onset of the extraction efficiency degradation is significantly smaller in this case since the larger confinement potentials reduce the electronic coupling. In type-II SLs with 1.0 eV bandgap, the extraction efficiency is ~95 % for a 6 nm period thickness, and strongly degraded for larger periods. The period thickness necessary to reach 100 % carrier collection efficiency is reduced to 4 nm.

Figure 4.16 shows the calculated electron and hole one-dimensional local density of states of two type-II SLs with the reduced 1.0 eV bandgap with two different period thickness, 3 and 6 nm.

Figure 4.16: Simulations of the local density of states (for $k_{\parallel}=0$) of 1.0 eV type-II SLs with 3 and 6 nm period thickness

In this series of type-II SLs with reduced bandgap, the dependence of the localization behavior with the period is equivalent to the previous type-II SLs series (see Figure 4.13). For the shortest 3 nm period SL, both electrons and holes are delocalized along the whole SL structure; for the 6 nm period SL, electrons are again delocalized, and holes are completely confined within the quantum wells.

Spectral PC density simulations to study the transport in the 1.0 eV bandgap SL structures after 1.2 eV monochromatic excitation are shown in Figure 4.17.

Figure 4.17: Simulations of the spectral current density under 1.2 eV monochromatic illumination of 1.0 eV type-II SLs with 3 and 6 nm period thickness.

As in the previous 1.2 eV type-II SLs series (see Figure 4.14), the transport mechanism is fast (quasi-ballistic) for electrons and holes in the 3 nm period SL, and in the 6 nm period SL the transport regime for holes have changed sequential tunneling with significant thermal phonon-mediated escape transport. However, unlike the previous series, sequential tunneling for electrons has already started in the 6 nm period structure. The overall effect is the general reduction in the extraction efficiency that has been observed in Figure 4.15.

4.3. Conclusions

In conclusion, strain balanced $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs grown on GaAs are shown to overcome some of the main problems inherent to the quaternary nature of the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ dilute nitride. The spatial separation of Sb and N atoms during epitaxial growth of the type-II SLs allows an accurate compositional and an effective bandgap control not achievable neither in $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$ type-I SLs nor in $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ thick layers, as well as an improved crystal quality and interface abruptness.

The type-II SLs structures allow additional tuning of the effective bandgap through the period thickness due to quantum confinement. Besides this, type-II SLs have some other advantages over bulk and type-I SL counterparts, such as long radiative carrier-lifetimes that can be controllably tuned through the period thickness.

Thick periods imply long radiative lifetimes, which in principle would be beneficial for carrier extraction efficiency. Moreover, to move towards low effective bandgaps, larger period thicknesses are also favored in principle.

However, NEGF simulations demonstrate that increasing the period thickness results in a change in the transport regime from quasi-ballistic to sequential tunneling and thermal escape, which reduces the extraction efficiency. For type-II SL structures with bandgap energies of 1.0 and 1.2 eV, the carrier extraction efficiency dramatically drops for period thickness thicker than 6 and 8 nm, respectively. The range of suitable period thickness is, however, much broader than in the type-I SL counterparts, in which the degradation of transport with thickness is much faster.

The results show that thick periods and, therefore, long radiative carrier lifetimes, are incompatible with efficient carrier transport in low bandgap (1–1.15) type-II SL structure; since transport is determinant for solar cell performance, the use of strain-balanced

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GaAs_{1-x}Sb_x/GaAs_{1-y}N_y type-II SLs with thin periods should be the best alternative for solar cells purposes.

5. GaAs(Sb)(N)-based solar cells

5.1. Introduction

As was discussed in Chapter 2, $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ is a suitable candidate for its implementation as 1.0–1.15 eV sub-cell in optimum GaAs/Ge-based MJSCs designs. Bulk layers of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ material have already been experimentally tested for MJSC applications [52,72,73,77,79–82,84]. However, as far as we know, the efficiencies achieved have not approached the predicted values, mainly due to difficulties in achieving high-quality material [92]. Several growth optimization strategies to increase the solar cell efficiency are currently under investigation, such as the optimization of V-V [64] or III-V [74] flux ratios, the growth temperature [75], or the use of growth rates higher than 1ML/s, which has been demonstrated to have a positive impact in other N-containing structures [219]. However, seizing on the results obtained in Chapter 4 regarding the possibilities offered by type-II SL engineering, a promising strategy for increasing solar cell efficiency would consist in replacing $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ bulk layers by $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs.

In this Chapter, the performance of two series of GaAs(Sb)(N)-based solar cells is analyzed, each one comprising at least one bulk sample and several different SL structures. The first series consists of samples with relatively “low” N and Sb contents (those necessary to reach ~1.15 eV bandgap), and the second consists of samples with relatively “high” N and Sb contents (to reach ~1.0 eV bandgap). It is well known that increasing the N content introduces a significant amount of point defects in GaAs-based diluted nitrides, such as N interstitials [154,155], Ga vacancies or interstitials associated to N [83,154,157,158] or As antisites [51,52,54,158], which is definitely one of the reasons that is complicating the successful application of dilute nitrides in MJSCs. Therefore, significant differences in the solar cell performance between the two series could be expected. This Chapter is based on results presented in articles [209,220,221], with permission of the corresponding journals.

The general description of the growth process of the samples studied in this Chapter can be found in Chapter 3, Section 3.1.2. The growth details of the active region of all the samples are summarized in Table B.2 in Appendix B. The description of every set of samples is at the beginning of each corresponding Section in this Chapter.

5.2. Results and discussion

5.2.1. Solar cells with ~ 1.15 eV bandgap

The active layers of the different samples have 816 nm thickness and are embedded in a p-i-n structure. The different layers consist on: a $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$ type-I SL with 12 nm period (*SL-I 12* sample), two $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ type-II SL with 12 nm (*SL-II 12* sample) and 6 nm (*SL-II 6* sample) period thickness, a bulk $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ layer grown at 1ML/s (*Bulk 1ML/s* sample), a bulk $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ layer grown at 2ML/s (*Bulk 2ML/s* sample), and a GaAs layer grown at 1 ML/s (*GaAs* sample) for reference. The Sb and N fluxes (corresponding to $\sim 1.5\%$ and $\sim 4.0\%$ nominal N and Sb contents, respectively) were chosen to obtain samples with a ~ 1.15 eV bandgap. N and Sb fluxes in the 2 ML/s sample were adjusted to provide the same N and Sb incorporation than in the 1 ML/s samples. All samples were processed as solar cell as described in Section 3.3. Details of the active layers are in Table B.2 in Appendix B.

5.2.1.1. Current-voltage curves and external quantum efficiency

JV measurements of a representative p-i-n diode from each sample taken under 1.2 eV monochromatic illumination are shown in Figure 5.1. The *GaAs* sample is missing in this graph because its bandgap energy is higher than the illumination energy.

Figure 5.1: Room temperature JV curves under 1.2 eV monochromatic illumination of one device from each sample: Bulk 1ML/s, Bulk 2ML/s, SL-I 12, SL-II 12 and SL-II 6.

Curves of diodes *Bulk 1ML/s* and *Bulk 2ML/s* are almost coincident, and both have a very similar slope in the negative bias region, which is also very similar in diode *SL-II 6*. The variation of the PC with reverse bias is much more significant in samples *SL-I 12* and *SL-II 12*. The PC at -3V is already saturated in the five analyzed devices, ensuring that this voltage can be considered to provide a complete carrier collection [186]. Then, the EQE at room temperature is taken at 0 V (short-circuit condition) and -3 V (complete carrier collection condition). EQE spectra of all the same diodes at both voltage values are shown in Figure 5.2.

Figure 5.2: Room temperature EQE spectra measured at 0 V (empty dots) and -3 V (filled dots) of one device of each sample: *Bulk 1ML/s* together with the GaAs reference sample, *Bulk 2ML/s*, *SL-I 12*, *SL-II 12* and *SL-II 6*.

An effective bandgap value for each device is extracted from the peak of the derivative of the EQE spectra at 0 V shown in Figure 5.2. The obtained bandgap energies are 1.10 eV for *Bulk 1ML/s*, 1.11 eV for *Bulk 2ML/s*, 1.11 eV for *SL-I 12*, 1.13 eV for *SL-II 12* and 1.19 eV for *SL-II 6*. These bandgap energy values are close to the intended 1.15 eV energy, though they are shifted to larger energies as the period thickness decreasing in the SLs samples because of the quantum confinement effect discussed in Section 4.2.2.2.

The carrier collection efficiency (CCE) is defined as the ratio between EQE at 0 V and EQE under complete carrier collection conditions.¹ For the *GaAs* device, there is no difference between the 0 V and -3 V curves, indicating 100 % CCE at 0 V, as expected. Nevertheless, there is a small enhancement of the EQE from 0 to -3 V in the bulk devices, which shows a peak CCE of ~95 % and ~97 % for *Bulk 1ML/s* and *Bulk 2ML/s*, respectively. This reduced CCE in the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ structure is likely an indication of non-radiative recombination at point defects or carrier localization in potential minima induced by strain and composition inhomogeneities in the quaternary alloy [222,223].

Moreover, for energies slightly above the bandgap, the EQE is larger in the $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ bulk layers than in the *GaAs* reference. This enhancement shall be attributed to the increase of the joint density of states reported for dilute nitrides [41–43] arising from a larger electron effective mass and thus a better matching to the hole band dispersion. *Bulk 2 ML/s* sample gives slightly higher EQE than *Bulk 1ML/s*.

Focusing on the 12 nm period SLs, EQE is larger in the *SL-II 12* sample than in the *SL-I 12*. This difference could be related to the benefits of type-II SLs which, thanks to an improved crystal and interface quality and their longer carrier lifetimes, experimentally show enhanced optical and transport properties. In the *SL-II 12* and *SL-I 12* devices the EQE increases with the reverse bias. The carrier extraction at 0 V is not efficient enough because the weak electronic coupling for a 12 nm period prevents carriers from tunneling through the SL barriers in the absence of an external electric field. This result agrees with the calculated carrier extraction efficiency drops for 1.2 eV bandgap 12 nm period type-I and type-II SLs (see Figure 4.15) and limits the potential applications of this kind of structures in solar cells.

However, the *SL-II 6* shows a larger EQE that is virtually the same at 0 V and at -3 V. This indicates improved carrier collection at 0 V and a considerable overlap of the SL minibands across the 6 nm period SL structure. In this SL sample, the difference in the measured EQE between -3 and 0 V is even smaller than in the bulk: the estimated CCE at 0 V (in peak values) are ~99 % for *SL-II 6* vs. ~95 % and ~97 % for *Bulk 1ML/s* and *Bulk 2ML/s*, respectively. Carrier transport is therefore improved as compared to the bulk

¹ It must be noticed that even complete carrier collection is a relative quantity, since, strictly speaking, it does not mean that all the photogenerated carriers are collected but just that we are collecting the maximum possible number of carriers for that particular structure. Therefore, there might be carrier losses, which cannot be suppressed by increasing the electric field.

alloy and complete carrier collection at 0 V is achieved. This improvement can be related to the reduction of non-radiative recombination, to carrier localization effects due to composition and strain inhomogeneities that arise in bulk alloys, as was observed by XRD material characterization of analog structures (see Section 4.2.1.1), or both.

It is important to note that though the total intrinsic region thickness is the same in all samples, the thickness of the absorbing material is twice in bulk than in SLs samples since bulk sample contains twice as much Sb and N than the SLs. Despite of that, the *Bulk 2ML/s* EQE peak at 0 V is only 21 % larger than EQE peak in the *SL-II 6* sample; a larger absorption coefficient or improved transport in the SL structure could be therefore inferred from this results.

The EQE measurements experimentally confirm that the electronic coupling and tunneling are strongly enhanced by reducing the period thickness from 12 to 6 nm in type-II SL, which correlates with the change in transport regime from sequential tunneling to quasi-ballistic predicted theoretically in Section 4.2.2.4.

5.2.1.2. Single-junction solar cell performance

For this series of samples, two diodes from each sample were measured under AM1.5G conditions. The JV curves of the best diode of each sample are shown in Figure 5.3. J_{SC} , V_{OC} , PCE , FF and W_{OC} corresponding values are shown in Table 5.1.

Figure 5.3: JV curves taken under AM1.5G standard illumination of one single-junction device of each sample: Bulk 1ML/s, Bulk 2ML/s, SL-I 12, SL-II 12, SL-II 6 and reference GaAs.

	J_{SC} (mA/cm ²)	V_{OC} (V)	PCE (%)	FF (%)	W_{OC} (V)
<i>Bulk 1ML/s</i>	26.62	0.39	6.07	65	0.71
<i>Bulk 2ML/s</i>	28.06	0.41	6.44	66	0.70
<i>SL-I 12</i>	5.72	0.37	1.00	47	0.74
<i>SL-II 12</i>	6.16	0.38	1.11	46	0.75
<i>SL-II 6</i>	22.69	0.45	6.08	61	0.74
<i>GaAs</i>	16.43	0.78	9.46	74	0.63

Table 5.1: Solar cell characteristic parameters of one device of each sample *Bulk 1ML/s*, *Bulk 2ML/s*, *SL-I 12*, *S-II 12*, *SL-II 6* and reference *GaAs* sample.

The PCE of the bulk solar cell grown at a faster rate is better than that of the standard growth rate counterpart (6.44 % vs. 6.07 %, respectively), because the *Bulk 2ML/s* has larger J_{SC} than the *Bulk 1ML/s* (28.06 mA/cm² vs. 26.62 mA/cm²) and also larger V_{OC} (0.41 V vs. 0.39 V). The use of higher growth rates could, therefore, be an adequate strategy to improve the performance of GaAs_{1-x-y}Sb_xN_y solar cells.

On the other hand, the performances of the *SL-I 12* and the *SL-II 12* samples are very similar, the type-II showing slightly better PCE values (1.00 % and 1.11 %, respectively). Both the *SL-I 12* and the *SL-II 12* have a very low J_{SC} , around 6 mA/cm², due to the carrier extraction problems described in the previous Section that occur for thick period SLs. They also have very similar V_{OC} (0.37 V and 0.38 V, respectively). The low V_{OC} values are probably not directly linked to the material quality of the devices, but to the same carrier collection problems which cause the J_{SC} reduction. Therefore, in the case of thick periods, carrier collection problems strongly degrade solar cell performance.

Nevertheless, the performance of the *SL-II 6* solar cell is comparable to those of the bulk samples, as a result of the better carrier extraction in SLs with reduced period thickness because of the formation of minibands (see Section 2.3.2). This device has a lower J_{SC} than the bulk samples (22.69 mA/cm²), and the V_{OC} (0.45 V) is bigger than in bulk samples due to the larger effective bandgap energy. The PCE (6.08 %) becomes close to the bulk ones.

W_{OC} is a better parameter than V_{OC} to compare the performance of solar cells with different bandgap energies. A low W_{OC} value points to a good solar cell quality, though as the V_{OC} parameter, it is not entirely independent of the J_{SC} . The W_{OC} values have been

calculated using bandgap values extracted from EQE (see Section 5.2.1.1). The lower W_{OC} values are provided by both bulk layers (0.70 V and 0.71 V, respectively), though both are still far from the W_{OC} of the GaAs cell (0.63 V), which can be used as reference of the best W_{OC} potentially achievable for these non-optimized solar cells. The three SL samples have higher W_{OC} values than bulk ones. The FF of devices are also better for bulk samples and are considerably reduced in 12 nm period SLs, though FF is partially recovered in the *SL-II 6* sample. A strong R_S is affecting the performance of the *SL-I 12* and the *SL-II 12* samples because of the difficult current flow caused by the absence of minibands.

In this series of solar cells with relatively “low” N and Sb concentration, SL structures do not give rise to an improved solar cell performance over bulk structures, not even SLs with short period thickness (6 nm), though in this case, the performance approaches that of the bulk case. Still, it has to be noticed that half the amount of N and Sb is used in the SLs. Also, it must be noticed that the poor performance is partially due to the un-optimized solar cell structures, as explained in Section 3.3, which is evident looking at the reduced values of the GaAs reference cell.

5.2.2. Solar cells with ~1.0 eV bandgap

Another series of three samples with 816 nm-thick active layer inserted in a p-i-n structure were grown and subsequently fabricated as solar cells as described in Section 3.3. According to the NEGF simulations (Section 4.2.2.4), to have a 1 eV single-junction cell with high extraction efficiency, SLs with type-II band alignment and period thickness below 6 nm must be chosen. Therefore, the new series of samples consists of two type-II SLs with 6 nm and 3 nm period thickness (*SC-SL 6* and *SC-SL 3* samples, respectively) and a bulk layer grown at 1ML/s (*SC-bulk*). The three samples were grown under slightly different N and Sb fluxes, to account with the carrier confinement caused by SL period thickness. To achieve a bandgap energy ~1.0 eV the N and Sb fluxes have been increased as compared to the previous samples to increase the N and Sb contents, to give ~2.3 % and ~6.2 % N and Sb nominal contents, respectively. All details of the active layers grown are shown in Table B.2, in Appendix B.

As already mentioned, the increase of N content with respect to previous solar cells series could give rise to changes in structural and optical material properties, which could strongly affect solar cell performance.

5.2.2.1. Current-voltage curves and external quantum efficiency

JV measurements of one representative p-i-n diode from each of these samples taken under 1.2 eV monochromatic illumination are shown in Figure 5.4. In this case, the current does not saturate for any device at -3 V. *SC-bulk* sample have a continuously increasing current with increasing negative bias, while the PC of *SC-SL 6* and *SC-SL 3* start to saturate at voltages close to -6 V.

Figure 5.4: Room temperature JV curves under 1.2 eV monochromatic illumination of one device from each sample: *SC-bulk*, *SC-SL 6* and *SC-SL 3*.

Unlike in the previous ~ 1.15 eV solar cells, complete carrier collection conditions are only achieved at voltages close -6 V for the SLs, and even larger for the bulk (if achieved at all). The EQE of the same three solar cells as a function of negative applied bias between 0 and -6 V are shown in Figure 5.5. The bandgap energies of the samples are in the 1.0 eV region, slightly shifted to higher energies in the SLs: the effective bandgap values extracted from the peak of the derivative of the EQE spectra at 0 V shown in Figure 5.5 are 1.00 eV for *SC-bulk*, 1.07 eV for *SC-SL 6* and 1.09 eV for *SC-SL 3*.

Figure 5.5: Room temperature EQE spectra of one device of each sample (SC-bulk, SC-SL 6 and SC-SL 3) taken at different voltages ranging from 0 V to -6 V. The top panels show the maximum of the EQE spectra as a function of reverse bias applied for the three solar cells.

There is a steady increase of the EQE with reverse bias in the three samples, which indicates a poor carrier collection efficiency at short-circuit conditions. Then, the three devices present low EQE and incomplete carrier collection at 0 V, in contrast with the previous series where bulk samples and 6 nm period thickness type-II SL solar cells virtually reach complete carrier collection at 0 V (see Figure 5.2). This difficulty in reaching complete carrier collection is in disagreement with the high collection efficiencies predicted by the model for 1.0 eV bandgap SLs with periods thinner than 6 nm (see Figure 4.15). Nevertheless, the EQE under short-circuit conditions is larger in the SLs than in the bulk

sample, the larger EQE corresponding to the thinner period SL. Remarkably, this is achieved by using half the amount of N and Sb in the SLs compared to the bulk.

The EQE peak of each spectrum versus the applied voltage is shown in Figure 5.5. In both SLs, the increase in EQE with the negative voltage finally saturates, implying that complete carrier collection is achieved under reverse bias, but at a much higher voltage than in previous series: around -5.5 V for *SC-SL 6* and -4.5 V for *SC-SL 3*. Nevertheless, EQE monotonically increases for the *SC-bulk* in the whole range of voltages measured. Complete carrier collection is therefore not achieved in the bulk sample in this range of voltages.

The larger EQE in the *SC-SL 3* solar cell for equivalent voltages and the faster saturation with reverse bias as compared to *SC-SL 6* can be explained in terms of the more substantial wavefunction overlap and density of states, which enhances the absorption coefficient (see Section 4.2.2.4) and the slightly higher extraction efficiency, as predicted by the NEGF model (see Figure 4.15). Nevertheless, the difference between the SL devices and the bulk ones must be due to different reasons, since a large density of states and 100 % extraction efficiency would be expected for a perfect bulk structure; the differences could, therefore, be related to the material quality.

Another important reason likely behind the improved EQE in the SLs is a reduced density of non-radiative recombination centers that are present in the *SC-bulk* because of the “high” N content introduced in this series of samples to reach ~ 1.0 eV bandgap. In the diluted nitrides grown by plasma-assisted MBE the way to produce active N is to create a plasma from ultra-pure N_2 (see Section 3.1). Nevertheless, several species coexist in the plasma: electrons, atomic nitrogen, diatomic nitrogen, and ionized nitrogen species [224,225]. The ionic species in the plasma reaching the growth surface could be a source of point defects and responsible for a degradation of the optical properties of the material as has been observed in $Ga_{1-x}In_xAs_{1-y}N_y$ [226]. Therefore, the fact that the amount of N incorporated as well as the plasma exposure time is halved in the SLs structures concerning the bulk one should result in a reduced defect density in the SLs.

The three samples were analyzed by TEM-related techniques that allow extracting the N and Sb distribution in the structure (see Section 3.2.5) to investigate their material quality. The left column in Figure 5.6 shows LAADF images in which N-containing regions appear with a brighter contrast, while the right column shows EDX maps of the Sb distribution in the very same region of the sample. Further analysis of the LAADF images demonstrates that in the SLs the presence of N is limited to the $GaAs_{1-y}N_y$ layers, while a significant Sb segregation to the $GaAs_{1-y}N_y$ layers is observed through EDX, as expected (see

Section 4.2.1.1). Remarkably, the Sb distribution looks more inhomogeneous in the bulk than in the SLs, with a larger density of Sb-rich clusters.

Figure 5.6: LAADF images highlighting the N distribution (brighter contrast) of samples SC-bulk, SC-SL 6 and SC-SL 3 (left column) and EDX maps of the Sb distribution on the very same region (right column). The in-plane Sb profiles averaged to the rectangles displayed are shown in Figure 5.7.

The alloy fluctuations can be quantified by plotting Sb content profiles in the in-plane direction, which shows a much larger standard deviation and variance in the bulk than in the SLs (Figure 5.7). The most homogeneous structure is the *SC-SL 6*, in which the spatial separation of N and Sb is larger than in the others, which demonstrates again that improved structural quality is obtained by avoiding the concomitant presence of N and Sb in the structure. The Sb clusters create potential wells in the VB that could lead to hole localization in those potential minima, slowing down the hole extraction process. Moreover, hole accumulation in the clusters could lead to Coulomb interaction effects that would also degrade transport.

Figure 5.7: In-plane Sb profiles of samples *SC-bulk*, *SC-SL 6* and *SC-SL 3* obtained from the EDX maps shown in Figure 5.6. The inset shows the average Sb content, the standard deviation and the variance of the measured profiles.

5.2.2.2. Single-junction solar cell performance

The reduced non-radiative recombination in the SLs should result in lower values of the dark saturation current (I_0) of the solar cell devices. Figure 5.8 shows dark IV curves of 10 to 15 devices in each sample in the positive voltage region.

Figure 5.8: Positive region of dark JV curves of 10 to 15 different devices of each sample: SC-bulk, SC-SL 6 and SC-SL 3.

An apparent reduction of the dark current is observed in both SL structures as compared to the bulk one. The average I_0 values estimated by fitting to a single diode model (Equation (2.1)) are $2.52 \cdot 10^{-3}$ mA/cm² for SC-bulk, $5.51 \cdot 10^{-4}$ mA/cm² for SC-SL 6 and $4.95 \cdot 10^{-4}$ mA/cm² for SC-SL 3. I_0 is very similar in the two SL samples and ~ 5 times lower than in the bulk sample. The reduced I_0 in the SLs structures confirms the effectiveness of the SL approach in reducing non-radiative recombination, which would have a strong impact on the performance of the solar cells under working conditions.

JV curves taken under AM1.5G standard conditions of a representative diode of each of the three structures are shown in Figure 5.9. In SC-bulk sample, five different devices were analyzed, and three in each SL structure. Table 5.2. shows the average values of the J_{SC} , V_{OC} , PCE , FF and W_{OC} of each sample, including the statistical errors.

Figure 5.9: JV curves under AM1.5G standard illumination of one representative device from each sample (SC-bulk, SC-SL 6 and SC-SL 3). The inset shows the average PCE of the three samples as a function of the bandgap energy, normalized to the value of the SC-bulk. The line indicates the small expected variation of PCE due to the change in bandgap energy.

	J_{SC} (mA/cm ²)	V_{OC} (V)	PCE (%)	FF (%)	W_{OC} (V)
SC-bulk	(4.9±0.5)	(0.25±0.01)	(0.68±0.06)	(56±3)	(0.75±0.01)
SC-SL 6	(6.4±0.7)	(0.30±0.01)	(0.99±0.08)	(50±3)	(0.77±0.01)
SC-SL 3	(9.5±0.2)	(0.32±0.01)	(1.59±0.06)	(53±1)	(0.77±0.01)

Table 5.2: Average values with its corresponding errors of the solar cell characteristic parameters of several diodes of each sample: five from SC-bulk, three from SC-SL 6 and three from SC-SL 3.

There is a clear increase in the average V_{OC} of the SLs as compared to the bulk sample: (0.30±0.01) V in the SC-SL 6 and (0.32±0.01) V in the SC-SL 3, versus (0.25±0.01) V in the SC-bulk. This difference could be mainly due to the larger effective bandgap. Nevertheless, there is also a significant enhancement in the J_{SC} of the SL devices despite the larger effective bandgap. The average J_{SC} increases from (4.9±0.5) mA/cm² in the

SC-bulk to (6.4 ± 0.7) mA/cm² in the *SC-SL 6* and (9.5 ± 0.2) mA/cm² in the *SC-SL 3*, respectively. The overall effect is a strong enhancement of *PCE*: it is enhanced by 46 % and 134 % in the *SC-SL 6* and the *SC-SL 3* over the *SC-bulk*, respectively. The inset of Figure 5.9 shows the average *PCE* of the three samples normalized to that of the *SC-bulk* as a function of the bandgap energy: the bandgap energy increment does not justify the substantial *PCE* increase in the SLs. Finally, the *FF* and *W_{OC}* average values are similar for the three solar cells, though slightly better for the bulk sample.

The efficiency improvement in the SLs over the bulk is mainly the result of the improved material quality (better composition homogeneity and reduced defect density), while the improvement among the SLs for thinner periods is related to a larger absorption coefficient and a better extraction efficiency due to a change in the transport regime caused by the period reduction, as was previously observed (see Figure 4.17). Again, the general poor performance is partially due to the un-optimized solar cell epitaxial and device structure, as explained in Section 3.3.

Remarkably, the situation is now very different than in the case of lower N and Sb contents. For the higher N and Sb contents required to reach 1 eV, the SL approach works very well and results in significant improvement of solar cell performance over the bulk. This enhancement of *PCE* in short period SLs is a favorable result that supports the advantages of strain-balanced GaAs_{1-x}Sb_x/GaAs_{1-y}N_y type-II SLs with thin periods for MJSCs.

5.3. Conclusions

In type-II GaAs_{1-x}Sb_x/GaAs_{1-y}N_y SLs with ~1.15 eV bandgap, solar cell characterization reveals serious performance issues for 12 nm period thickness SLs as compared to 6 nm period SLs. Such transport problems are related to an incomplete carrier collection at short-circuit conditions for long period thickness, which agrees with the NEGF simulations results presented in the previous Chapter.

The results show that thick periods SLs (involving longer radiative carrier lifetimes) are incompatible with a high extraction efficiency. Both absorption (enhanced for stronger electronic coupling) and carrier extraction are maximized for thin-period SLs.

On the one hand, the type-II SL with ~1.15 eV bandgap and 6 nm period thickness has a slightly worse solar cell performance than bulk solar cells. Therefore, the SL approach is not advantageous in terms of solar cell performance. However, type-II SLs have still other

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benefits over the bulk, like the use of half the amount of N and Sb, accurate composition and strain balance control and fine bandgap adjustment through period thickness, as addressed in the previous Chapter.

On the other hand, in type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs with smaller bandgap (~ 1.0 eV), which require higher N and Sb contents, 3 and 6 nm period thickness SLs provide considerable better solar cell performance than an equivalent bulk solar cell. The detrimental effects of the “high” content in the material properties degrade the solar cell performance but, in this scenario, the SL approach results very useful, providing a *PCE* enhancement of 134 % over the bulk for thin periods of 3 nm. This improvement is partially due to a reduced composition inhomogeneity and recombination at N-induced defects. These results make short period $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs a potentially better alternative to thick $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ layers to be integrated as a 1.0 eV layer in a monolithically grown GaAs/Ge based MJSC.

6. Effect of rapid thermal annealing in GaAs(Sb)(N)-based solar cells

6.1. Introduction

As discussed in Chapter 2, the introduction of small quantities of N in a GaAs matrix to create a dilute nitride material strongly modify their properties. In Chapter 3, Section 3.2.1.1, it was stated that even very low N concentration can give rise to compositional inhomogeneities and N-related defects in the alloy, which induce carrier localization effects and non-radiative recombination centers that undermine the optical properties and impact negatively on the performance of the dilute nitride solar cells, including the GaAs(Sb)(N)-based ones.

Apart from the growth-based strategies to increase GaAs(Sb)(N)-based solar cell efficiencies mentioned in the introduction of the previous Chapter, a post-growth RTA treatment could be useful to improve the structural, optical and electrical properties of $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ alloys, yielding to a solar cell efficiency improvement. The beneficial effect of RTA on $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ and other dilute nitrides has been discussed in Chapter 3, Section 3.5.1. The improvement in material properties upon annealing has been usually attributed to the elimination of non-radiative recombination centers, but the possible effect of sub-bandgap N-related radiative states has not been investigated to date. Indeed, apart from the band-to-band PL peak and the low energy tail, a different PL emission band at lower energies has been observed in some cases in both $\text{GaAs}_{1-y}\text{N}_y$ [164,165,227] and $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ [193,201,228] and attributed to different causes. Nevertheless, the actual origin of the low energy emission band observed remains unknown, as well as its precise dependence on the N and Sb contents and its evolution upon RTA. Moreover, as far as we know, it has never been directly analyzed in correlation to solar cell performance.

In this Chapter, first, the sub-bandgap emission in $\text{GaAs}_{1-y}\text{N}_y$, $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ layers with different N and Sb contents is analyzed. Second, the effect of RTA on the optical and structural properties of the same p-i-n structures with “low” N and Sb contents that were employed to fabricate the ~1.15 eV solar cells that were discussed in

Section 5.2.1 is studied. Then new solar cells are fabricated from annealed pieces of the samples (RTA devices). The device characterization is correlated with modifications in material properties upon annealing and particularly on the intensity of the N-related sub-bandgap luminescence. The performance of RTA devices is compared with the performance of as-grown devices shown in Section 5.2.1. Finally, an analog study is performed on the p-i-n samples with “high” N and Sb contents that were used to fabricate ~1.0 eV solar cells discussed in Section 5.2.2. In this series, as-grown solar cells have shown hindered solar cell performance caused by the relatively “high” N content. The first part of this Chapter is based on the articles [182,220], the second is still unpublished.

The general description of the growth process of the samples studied in this Chapter can be found in Chapter 3, Section 3.1.2. The growth details of the active region of all the samples are summarized in Table B.3 and Table B.4 in Appendix B. The description of every set of samples is at the beginning of each corresponding Section in this Chapter.

6.2. Results and discussion

6.2.1. N-related deep radiative defects

In order to investigate the presence of optically active defects in $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ alloys that could affect the performance of solar cells, a first series of samples was grown: two ternary bulk samples, the first one containing only Sb (*GaAsSb* sample) and the second one containing only N (*GaAsN* sample) and one bulk quaternary sample containing both Sb and N (*GaAsSbN* sample). These three samples have a 200 nm thick active region and were grown under the same Sb and N fluxes, which corresponds to nominal contents of 1.1 % N and 2.2 % Sb (see Table B.3 in Appendix B).

15 K PL measurements of this set of samples are shown in Figure 6.1 a). The PL spectrum from a GaAs substrate (Si-doped, n^+) is also included as reference. The *GaAsN* and *GaAsSbN* samples show a dominant emission peak corresponding to the band-to-band luminescence at 1.24 and 1.20 eV, respectively, and a broad band emission at lower energies, from about 0.75 eV to around 1.05 eV, more intense in the ternary *GaAsN* than in the *GaAsSbN* sample. The *GaAsSb* sample shows a sharp band-to-band luminescence emission at 1.48 eV. Its low relative intensity could be attributed to a non-optimal growth temperature [229–231], which was indeed optimized for N-containing structures.

Figure 6.1: 15 K PL spectra of different series of samples. Features observed in the 0.9 eV region in every spectrum are related to water absorption in the air. a) Spectra of GaAsSb, GaAsN, and GaAsSbN samples grown using the same Sb and N fluxes along with the spectrum of a GaAs n^+ substrate as a reference. b) Spectra of ternary GaAs_{1-y}N_y samples with different N contents. c) Spectra of quaternary GaAs_{1-x-y}Sb_xN_y samples with fixed N content and increasing Sb contents.

The low energy broad PL emission observed in GaAsN and GaAsSbN is not present in GaAsSb or GaAs substrate spectra. The peak at ~1.15 eV in those samples is well known in Si-doped GaAs and attributed to Si_{Ga}-V_{Ga} complexes [232,233], whereas the emission at lower energies in the 1 eV region is attributed to Si_{Ga}-Si_{As} complexes [233,234]. The peak

at ~ 1.35 eV, visible in all the samples, comes from V_{Ga} defects [232] and the peak at ~ 1.49 eV is due to the near band edge Si donor to C acceptor pair recombination [232]. Therefore, all these peaks have their origin in the Si-doped GaAs n^+ substrate.

The evolution of the low energy band with the N content was investigated through a second series of three samples with an active layer consisting on 200 nm-thick $\text{GaAs}_{1-y}\text{N}_y$ layers with 0.4 %, 0.6 % and 0.9 % of N respectively, contents which have been determined through XRD measurements, along with the previous GaAsN sample with 1.1 % N. All the growth parameters of the active layers of these samples are described in Table B.3 in Appendix B. As shown in Figure 6.1 b), the sub-bandgap emission intensity increases with the N content in the structure. Remarkably, the peak energy of this band is not shifted with the N content, while its PL increases becoming even similar to that of the band-to-band emission for N contents around 1 %. The apparent dips in the luminescence of the band-to-band edge PL band at ~ 1.2 eV and ~ 1.35 eV (the latter visible only in the sample with 0.4 % N) are likely due to the convolution with the substrate peaks at 1.15 and 1.35 eV, respectively.

At the other end, the noticeable reduction of the sub-bandgap emission observed in Figure 6.1 a) with the addition of Sb was also analyzed in a third set of samples. In this third series of samples, the N content in the active region is fixed to 1.8 %, while the Sb flux increases, leading to Sb contents from around 3 % to 10 %. All the growth parameters of the active layers of these samples are described in Table B.3, in Appendix B. As shown in Figure 6.1 c), the low energy band emission intensity progressively decreases with the increasing Sb content in the alloy. Ultimately, for the highest Sb content, the broad band emission virtually disappears (the peak appearing at 0.96 eV corresponds to the band-to-band emission of the sample).

There is, therefore, a significant density of states within the bandgap at 450 meV below the CB in N-containing samples. The highest energy states of this deep band overlap with band tail states typically observed in diluted nitrides, since the PL signal does not go to zero between the two peaks. This emission band can be attributed to the existence of N-induced radiative defects and not to the presence of Sb-related defects, being its intensity directly related to the N concentration. On the contrary, Sb seems to help to reduce the N-induced defect density, as the inclusion of Sb to form the quaternary GaAsSbN reduces the emission intensity related to such N-induced defects. Indeed, Sb contents of ~ 10 % are enough to virtually suppress the PL emission for an N content close to 2 %.

Evidence of the defect origin of the sub-bandgap emission comes from the excitation power dependence of the PL, which is shown in Figure 6.2 a) for sample GaAsN. The laser power excitation was varied by two orders of magnitude. The low-bandgap emission peak (N peak) is the most intense at low excitation powers, while the PL spectrum is mostly dominated by the band-to-band peak (GAP peak) at high excitation powers. The trend to saturate of the N peak with the laser power is typical of a defect level emission; at high excitation power, the defects that origin this emission are fully populated. On the other hand, the increment of the GAP peak intensity with the power is characteristic of a free-carrier recombination process.

Figure 6.2: a) 15 K PL spectra of sample GaAsN taken with different laser excitation powers, between 0.03 and 2.7 mW. b) II of the GAP peak and N-peak as a function of the laser excitation power along with the linear fits of each peak emission.

It has been demonstrated that the nature of the recombination process can be inferred from its power dependence according to an $I \sim P^k$ law [235], where I is the luminescence intensity and P is the laser power. A k value between 1 and 2 indicates free-carrier (exciton or band-to-band) recombination; meanwhile, a k value lower than 1 points to defect-related recombination, such as donor-acceptor pair transitions. The II of each PL peak shown in Figure 6.2 a) as a function of the laser power excitation, are presented in Figure 6.2 b) in a log-log plot. As a first approximation, the k values correspond with the slopes of the linear fits performed, which are (1.21 ± 0.05) for the GAP peak and (0.88 ± 0.04) for the N peak. This results support the defect-related recombination origin of the N peak.

Similar low energy emission bands to these have been previously reported on GaAs_{1-y}N_y and GaAs_{1-x-y}Sb_xN_y layers. Its possible origin has been ascribed to the existence of structural

defects because of the incorporation of N atoms into the host matrix [164,165,193,227], defects associated with Sb presence [201] or residual impurities [228]. However, the exact nature of this emission has still not been determined. There are also other works in which this band is not observed; this could sometimes be due to the high Sb contents [236], or even to different growth conditions (defect formation in diluted nitrides is strongly affected by the growth conditions [54]).

6.2.2. Annealing of solar cells with ~1.15 eV bandgap

The analyzed samples are the same ones described in Section 5.2.1 except for sample *SL-I 12*, that was not included in the RTA study. In this series, the nominal contents are ~1.5 % N and ~4 % Sb, and the bandgap energies of the samples are around 1.15 eV.

6.2.2.1. Effect of annealing on luminescence

Three different temperatures, 750, 800 and 850 °C, were employed to anneal different pieces of each structure. These temperatures are within the range that has been found to improve the quality of dilute nitride materials [56,188,191,196,197] and, particularly, GaAs_{1-x-y}Sb_xN_y [72,78]. PL measurements before and after RTA in the very same sample pieces were used to test the three RTA temperatures.

PL spectra in all samples present the main peak corresponding to the bandgap energy (GAP peak) and the sub-bandgap broad band attributed to N-related states (N peak) as those of Figure 6.1. RTA treatment has a strong influence on the PL properties. To choose the optimum annealing temperature for device processing, three PL characteristics of the band-to-band peak are taking into account: increment of peak intensity (ΔI_{GAP}), reduction of FWHM ($\Delta \text{FWHM}_{\text{GAP}}$) and increment of Π ($\Delta \Pi_{\text{GAP}}$). Then, the selection of the final temperature consists of a tradeoff between the three criteria. The data for all the samples at the three temperatures is shown in Figure 6.3. In the case of the bulk samples, it must be noticed that the I_{GAP} and Π_{GAP} decrease for all the three analyzed annealing temperatures. This unexpected reduction of PL intensity is discussed later. In these samples, the temperature leading to the larger reduction of FWHM_{GAP} is chosen and, when compatible, leading to the smaller reduction of I_{GAP} and Π_{GAP} . The chosen temperature for device processing is 800°C for the four samples.

Figure 6.3: ΔI_{GAP} (left column), $\Delta FWHM_{GAP}$ (central column) and ΔII_{GAP} (right column) obtained by comparing band-to-band PL peaks of as-grown and RTA samples. Each row corresponds to a different sample (Bulk 1ML/s, Bulk 2ML/s, SL-II 12 and SL-II 6). RTA process was performed at 750, 800 and 850 °C; three different pieces of each sample were used, one for each temperature.

15 K PL spectra taken over the same sample pieces before and after RTA at 800 °C (as-grown and RTA, respectively) are represented in Figure 6.4. II_{GAP} , II_N and $FWHM_{GAP}$

values of each as-grown and RTA sample are presented in Table 6.1, as well as the blueshift of the main peak after RTA ($\text{Blueshift}_{\text{GAP}}$).

Figure 6.4: 15 K PL spectra of samples Bulk 1ML/s, Bulk 2ML/s, SL-II 12 and SL-II 6 as-grown (blue lines) and after RTA at 800 °C (red lines).

	II_{GAP} (arb. units)		FWHM_{GAP} (meV)		$\text{Blueshift}_{\text{GAP}}$ (meV)	II_{N} (arb units)	
	a-g	RTA	a-g	RTA		a-g	RTA
Bulk 1ML/s	0.574	0.157	69	36	45	0.512	0.136
Bulk 2ML/s	0.484	0.170	78	56	50	0.539	0.214
SL-II 12	0.960	1.379	36	22	50	0.625	0.159
SL-II 6	0.328	0.381	84	44	73	0.893	0.333

Table 6.1: Quantitative analysis of the PL spectra. II_{GAP} , FWHM_{GAP} , $\text{Blueshift}_{\text{GAP}}$ and II_{N} of samples Bulk 1ML/s, Bulk 2ML/s, SL-II 12 and SL-II 6, either as-grown and after RTA.

Regarding the as-grown samples, the *Bulk 1ML/s* has a slightly more intense GAP peak than the *Bulk 2ML/s* sample, but both have similar N peak emission in terms of shape and II. On the other hand, the *SL-II 12* has by far the most intense GAP peak, which could be the result of better crystal quality and better quantum confinement [209], as shown in Section 4.2.1.2. The sample *SL-II 6* has the less intense GAP peak but the strongest N peak in terms of II. Focusing on the N-related emission band, its II is similar in both bulk samples and larger in SL samples, which agrees with the Sb-induced reduction of the N-related sub-bandgap emission mentioned in Section 6.2.1: since N and Sb are spatially separated in the SLs, a stronger emission would be expected from the pure $\text{GaAs}_{1-y}\text{N}_y$ layers than from $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$.

A blueshift of the band-to-band peak is observed after RTA in all spectra. PL blueshift induced by annealing is a commonly observed effect in dilute nitrides and has been attributed to different effects, from interdiffusion mechanisms to a modification of the atomic configuration, as was explained in Section 3.5.1. Blueshifts with values very similar to those obtained here have also been observed in $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ bulk and QW structures after annealing process and attributed to atomic As/Sb or As/N interdiffusion [201], reduction of the density of tail-states present in dilute nitrides, without any change in the composition (neglecting the atomic diffusion) [92,193,202] or material reorganization related with second-neighborhood atomic recombination of Sb-N pairs, resulting in more uniform structural arrangement [195]. Remarkably, the blueshift in all cited works is always accompanied by a band-to-band PL intensity increasing and a FWHM decreasing.

In the present case, the reduction of the FWHM of the main peak after RTA in all samples points out to the removal of clusters, improving the homogeneity of the N and Sb distribution. However, though the main PL peak intensity increases after RTA in SL samples (especially in *SL-II 12* sample), this does not happen in bulk samples. The reduction of the band-to-band emission intensity in bulk structures after RTA is an unexpected result. The N peak emission is reduced after annealing in all samples, in agreement with previous observations [193,201]. Moreover, the reduction of both peaks (GAP peak and N peak, respectively) in bulk samples after RTA is very similar, as if they were originated by increased non-radiative recombination, contrary to what would be expected [155,189,190]. A reduced carrier localization due to potential fluctuations after RTA could also have something to do with the observed behavior in bulk samples, while recombination from localized states would be strongly reduced in the SLs due to the spatial separation of electrons and holes in the potential wells. Remarkably, despite the different behavior of the GAP peak after annealing in the bulk and SLs, the RTA process induces a similar reduction of the N peak on every sample. The strong II_N reduction after RTA points to a significant

reduction of the density of deep sub-bandgap states and, therefore, to the annihilation of N-related radiative defects.

6.2.2.2. Effect of annealing on structural properties

XRD measurements were performed on the same pieces than PL measurements, before and after the RTA process (as grown and RTA, respectively). Figure 6.5 shows two representative cases, the $\omega - 2\theta$ scans around the (004) GaAs Bragg reflection of the *Bulk 1ML/s* and *SL-II 12* samples. The central peak corresponds to the GaAs substrate.

Figure 6.5: $\omega - 2\theta$ scans performed on the *Bulk 1ML/s* and *SL-II 12* samples, both as-grown (solid lines) and after RTA (dashed lines).

The position of the active layer diffraction peak (which in the *SL-II 12* diffractogram overlaps with the substrate peak because of lattice matching) does not undergo any variation after the RTA process in the SLs, which means that the average N-Sb composition in the lattice structure remains unaltered. A minimal shift to larger angles (indicating an enhanced tensile strain) is observed in the bulk sample, whose origin remains unknown for the moment.

Furthermore, the diffraction peak of the active layer becomes sharper after the annealing process, pointing out to an improvement in crystal quality through the thermal treatment.

Focusing on *SL-II 12*, the satellite peaks that characterize the SL periodicity are preserved after annealing: the SL periodicity and the well-barrier interfaces have not been deteriorated during the annealing process. Therefore, no significant Sb-N intermixing between adjacent layers, that would ultimately transform the SL in a bulk structure takes place during RTA.

Structural characterization is completed with TEM analysis. DF 002 images (not shown) indicate that all the samples are pseudomorphic, with no evidence of plastic relaxation through dislocations or any other sort of extended defects. Figure 6.6 a) shows LAADF images of *SL-II 12* sample as-grown and RTA. The N-containing layers are easily identified since they present a much brighter contrast than the $\text{GaAs}_{1-x}\text{Sb}_x$ layers (see Section 3.2.5) [182,210]. Abrupt interfaces with symmetrical and squared N profiles along the growth direction can be seen in both samples, which points to a very low segregation of N outside the $\text{GaAs}_{1-y}\text{N}_y$ layers even after the RTA.

Figure 6.6: a) LAADF images of the *SL-II 12* sample, as-grown and RTA. b) EDX maps of the Sb distribution of the *SL-II 12* sample, as-grown and RTA. c) Sb content profiles of the *SL-II 12* sample, as-grown (orange line) and RTA (green line) obtained from the EDX maps along the growth direction and the in-plane direction. The Sb profiles along the growth direction are obtained using an integration width of 80 nm. In the profiles along the in-plane direction, the integration width is 6 nm, so the profile is the average of a single $\text{GaAs}_{1-x}\text{Sb}_x$ layer.

Figure 6.6 b) shows EDX maps of the Sb elemental distribution taken over the same regions. These maps reveal the existence of a higher density of clusters with an Sb

composition up to 7.0 % in the $\text{GaAs}_{1-x}\text{Sb}_x$ layers of the as-grown sample. Instead, RTA sample maps point towards a more homogenous Sb distribution with a reduction of the Sb cluster density. To quantitatively compare the number and size of the Sb clusters, equivalent areas of 3700 nm^2 in the Sb EDX maps corresponding to the as-grown and the RTA structures were examined, with the criteria of consider as clusters Sb-accumulation regions larger than 2 nm^2 . Both the number of clusters and the cluster's total area are doubled in the as-grown sample as compared to the RTA one (36 versus 18 and 120 nm^2 versus 50 nm^2 , respectively). [182].

Sb content profiles along the growth and in-plane directions are plotted in Figure 6.6 c). Remarkably, the Sb profiles along the growth direction barely exhibit any difference between as-grown and RTA samples. These measurements demonstrate that neither Sb nor N are further segregated along the growth direction after RTA, maintaining the original profiles. On the other hand, the Sb profile along in-plane direction within one of the $\text{GaAs}_{1-x}\text{Sb}_x$ layers in the as-grown sample show a high oscillation of the Sb content between 2.5 % and 6.5 %- In the RTA sample, an analog profile show a reduced Sb content oscillation, varying only from 3.5 % to 5.5 %. The average Sb contents and the corresponding standard deviations extracted from these data are 4.5 % and 0.7 % for the *as-grown SL-II 12* sample and 4.6 % and 0.4 % for the RTA *SL-II 12* sample, which confirms the significant homogenization of the Sb composition obtained after annealing. The average Sb contents and standard deviations calculated through in-plane profiles taken at different $\text{GaAs}_{1-x}\text{Sb}_x$ layers are very similar.

6.2.2.3. Effect of annealing on single-junction solar cell performance

The same pieces of samples *Bulk 1ML/s*, *Bulk 2ML/s*, *SL-II 12* and *SL-II 6* that were analyzed by PL and XRD before and after RTA at 800°C in Section 6.2.2.1 and Section 6.2.2.2. were processed as solar cells.

The room temperature EQE at 0 V of a representative p-i-n diode from each RTA sample along with the EQE at 0 V of the as-grown diodes already shown in Figure 5.2 are shown in Figure 6.7.

Figure 6.7: Room temperature EQE at 0 V of one diode of each RTA sample: Bulk 1ML/s, Bulk 2ML/s, SL-II 12 and SL-II 6 (dashed lines) along with the room temperature EQE at 0 V of one diode of each equivalent as-grown samples (solid lines).

There is a similar reduction of the EQE peak after annealing of $\sim 19\%$ (in absolute terms) in all samples except in *SL-II 12*. This EQE reduction could be related to the existence of higher non-radiative recombination caused by the improvements in the alloy homogeneity. In *SL-II 12* sample, the EQE of the as-grown solar cell is already much lower than in the others. This short EQE is due to transport problems caused by carrier localization in the QWs which makes this structure inadequate as a solar cell, as was discussed in Sections 5.2.1.2. and 5.2.2.2. The large period thickness prevents electronic coupling and miniband formation, which results in strong carrier localization and efficient recombination in the QWs. The fact that the PL of this structure is much more intense than that of the others supports this idea (see Figure 6.4). The obtained bandgap energies from the peak of the derivative of the EQE spectra at 0 V shown in Figure 6.7 are 1.13 eV for *Bulk 1ML/s*, 1.15 eV for *Bulk 2ML/s*, 1.18 eV for *SL-II 12* and 1.22 eV for *SL-II 6*; the blueshift in the onset of the EQE spectra after RTA is evident in all cases (30, 40, 50 and 30 meV respectively). The slope of the absorption edge is not modified significantly, indicating that RTA is not strongly affecting the density of band tail states in the structures.

For this series of samples, two diodes from each annealed sample were measured under AM1.5G standard conditions to investigate the impact of RTA on solar cell performance. The JV curves of the best diode of each sample are shown in Figure 6.8. J_{sc} , V_{oc} , PCE , FF and W_{oc} values of each device are shown in Table 6.2. An RTA GaAs device from the same GaAs sample presented in Section 5.2.1 is included for reference.

Figure 6.8: JV curves under AM1.5G standard illumination of one diode of each RTA sample: Bulk 1ML/s, Bulk 2ML/s, SL-II 12, SL-II 6 and reference GaAs.

	J_{sc} (mA/cm ²)	V_{oc} (V)	PCE (%)	FF (%)	W_{oc} (V)
Bulk 1ML/s RTA	17.95	0.51	5.73	63	0.62
Bulk 2ML/s RTA	15.57	0.52	5.24	65	0.63
SL-II 12 RTA	2.50	0.50	0.70	56	0.68
SL-II 6 RTA	10.12	0.59	4.07	67	0.63
GaAs	20.21	0.73	11.14	76	0.68

Table 6.2: Solar cell characteristic parameters of one device of each RTA sample Bulk 1ML/s, Bulk 2ML/s, SL-II 12, SL-II 6 and reference GaAs sample.

The *Bulk 1ML/s RTA* sample has slightly better J_{SC} than the *Bulk 2ML/s RTA* sample (17.95 mA/cm² and 15.57 mA/cm², respectively) but slightly worse V_{OC} (0.51 V vs. 0.52 V, respectively), which made PCE to be similar in both samples (5.73 % and 5.24 %, respectively). Both RTA bulk solar cells show a better performance than the SL cells: the *SL-II 12 RTA* sample has a very low PCE (0.70 %) because the small J_{SC} (2.50 mA/cm²), though the V_{OC} is comparable to the ones of the bulk samples (0.50 V). In the *SL-II 6 RTA* sample, the J_{SC} is small when compared to those of the bulk samples (10.12 mA/cm²), but its bigger V_{OC} (0.59 V) make its PCE (4.07 %) approaching the PCE of the RTA bulk samples. The FF and the W_{OC} values of *Bulk 1ML/s RTA*, *Bulk 2ML/s RTA* and *SL-II 6 RTA* are comparable, being better for the RTA short period SL sample. It must be noticed again that the performances are easily improvable by a proper solar cell design (see Section 3.3).

The solar cell characteristic values of these RTA solar cells (presented in Table 6.2) should be compared with the values provided by the equivalent as-grown solar cells (presented in Table 5.1).

The J_{SC} values are reduced after RTA, as expected from the EQE results (Figure 6.7), but not in the *GaAs* reference sample. The relative reductions are -33 %, -45 %, -56 % and -55 % for *Bulk 1ML/s*, *Bulk 2ML/s*, *SL-II 12* and *SL-II 6* structures, respectively, and the relative increment for the *GaAs* sample is 23 %. The origin of this reduction of the J_{SC} is still under investigation, but it could be related to the elimination of the optically active deep states and the observed larger bandgap in the RTA samples, which results in a lower J_{SC} . Another possible explanation would be the presence of Be diffusion to the intrinsic region as a result of RTA [237], which would reduce the thickness of the intrinsic region in the p-i-n junction and, therefore, the photogenerated current. However, the fact that the J_{SC} does not decrease in the *GaAs RTA* solar cell, having precisely the same p-i-n structure, rules out this possibility. In any case, the J_{SC} reduction after RTA is a potential problem for current matching in MJSCs. Nevertheless, this could be in principle solved by making thicker absorber layers. Indeed, the EQE or J_{SC} of similar GaAs_{1-x-y}Sb_xN_y and Ga_{1-x}In_xAs_{1-y}N_y:Sb solar cells has been shown to increase with the active layer thickness up to 1 μ m in as-grown structures [78,238], and even up to 3 μ m in annealed solar cells [56].

The V_{OC} of all the GaAs(Sb)(N)-based structures increases noticeably after RTA, while that of the *GaAs* sample slightly decreases. The relative increment is similar in all structures: 31 %, 27 %, 32 % and 31 % for *bulk 1ML/s*, *bulk 2ML/s*, *SL-II 12* and *SL-II 6*, respectively. The relative reduction in the *GaAs* is -6 %. A similar V_{OC} increase (around 31 %) was obtained after an optimum annealing process in bulk Ga_{1-x}In_xAs_{1-y}N_y:Sb solar cells [56], being attributed to the elimination of non-radiative recombination centers.

Because of the strong J_{SC} reduction, the PCE decreases after annealing. Regarding the FF , the values are similar before and after RTA for both bulk samples, but significantly increases in SL samples: 22 % in *SL-II 12* and 10 % in *SL-II 6*. The highest value of the FF (67 %) is obtained for the *RTA SL-II 6* device. Finally, the W_{OC} is reduced after RTA, but no in the *GaAs* solar cell.

Figure 6.9 shows the difference in Π_N from PL spectra (Table 6.1) between as-grown and RTA samples ($\Delta\Pi_N$) and the difference in W_{OC} values (Table 5.1 and Table 6.2) between as-grown and RTA devices (ΔW_{OC}). ΔW_{OC} already accounts for the blueshift observed after RTA. A correlation seems to exist between $\Delta\Pi_N$ and ΔW_{OC} for each type of cell. This fact suggests that the increase of the V_{OC} after RTA is related to the reduction of the density of N-related deep radiative defects. There is no correlation with the evolution of the intensity of the band-to-band PL peak, which would typically be affected by non-radiative recombination. Indeed, Π_{GAP} decreases in the bulk samples. Although the reduction of non-radiative defects could also contribute to the increase of the V_{OC} , the present results indicate that it could not be the main factor. Instead, the reduction of N-related radiative defects upon annealing results in a reduced radiative recombination of carriers photogenerated above the bandgap, as it is evidenced in the PL by the reduced Π_N after RTA. Moreover, the reduction of the density of deep radiative levels would raise the electron quasi-Fermi level for a given density of photogenerated carriers, resulting in a larger V_{OC} . Besides this, the composition homogenization observed after RTA could also contribute to enhance the V_{OC} by reducing carrier trapping (and eventually radiative recombination) at the potential wells.

Figure 6.9: Difference in Π_N between RTA and equivalent as-grown samples (right axis) and difference in W_{OC} between RTA and equivalent as-grown samples (left axis) for samples Bulk 1ML/s, Bulk 2ML/s, SL-II 12 and SL-II 6.

The W_{OC} values of the as-grown and RTA devices of samples *Bulk 1ML/s*, *Bulk 2ML/s*, *SL-II 12* and *SL-II 6* (Table 5.1 and Table 6.2) are represented in Figure 6.10 as a function of their respective bandgap energies, together with that of the as-grown and RTA un-optimized reference *GaAs* solar cells. A low W_{OC} value is indicative of a good solar cell material quality; therefore, W_{OC} values close to the dotted lines would indicate a material quality similar to that of the *GaAs*. The W_{OC} values of the as-grown GaAs(Sb)(N)-based solar cells are all above the *GaAs* reference line. The high W_{OC} values are typical of the diluted nitrides, which deviate from the approximately constant W_{OC} obtained for many other materials; indeed, W_{OC} values ~ 200 mV larger than those of *GaAs* are obtained for $Ga_{1-x}In_xAs_{1-y}N_y$ with a 1.05 eV bandgap [30]. Nevertheless, the W_{OC} parameter is significantly reduced when the structure is annealed because of the beneficial effects of the thermal treatment shown previously. The two bulk samples and the *SL-II 6* have slightly lower W_{OC} values than the reference as-grown *GaAs* when annealed, indicating comparable material quality to *GaAs*, and clearly better W_{OC} than the RTA *GaAs* cell. The higher W_{OC} values of the structure *SL-I 12* before and after RTA are due to the low J_{SC} , not to a worse material quality.

Figure 6.10: W_{OC} as a function of the bandgap energy of samples *Bulk 1ML/s*, *Bulk 2ML/s*, *SL-II 12* and *SL-II 6*, as-grown (blue dots) and RTA (red triangles), along with W_{OC} values of other published $GaAs_{1-x}Sb_xN_y$ solar cells (green squares). The W_{OC} values of the as-grown and RTA *GaAs* reference samples are also shown. Dotted lines represents W_{OC} values indicating a material quality similar to that of *GaAs*

Figure 6.10 also shows W_{OC} values of $GaAs_{1-x}Sb_xN_y$ solar cells found in the literature. Some of them (cells from refs. [77,78,82]) have values lower than those obtained here, but they have window layer and anti-reflective coating [78,82] or, at least, a window layer [77]. Therefore, although no reference GaAs cell is studied in those papers, it is reasonable to think that the W_{OC} value of an equivalent GaAs cell would be lower than ours (see values reported in [239], for example). W_{OC} values of these solar cells would be reduced by using a more adequate solar cell structure. Nevertheless, the fact that W_{OC} value of the GaAs reference solar cell have been reached by the RTA solar cells suggests that, for these “low” N and Sb contents, the RTA process allows bringing the W_{OC} of the GaAs(Sb)(N)-based cells to the level of the rest of high-quality materials. This is a promising result highlighting that integration of such structures as efficient 1.15 eV sub-cells in lattice-matched GaAs/Ge-based MJSCs should be possible after the appropriate annealing cycle.

6.2.3. Annealing of solar cells with ~1.0 eV bandgap

The analyzed samples are the same ones described in Section 5.2.2. The nominal contents are ~2.3 % N and ~6.2 % Sb, and the bandgap energy of the samples is close to 1.0 eV. In this series of samples, the nominal N content is increased by 0.8 % with respect to the previous series, which is a significant increment when it comes to dilute nitrides. We have already shown in Chapter 5 that this larger N content leads to a significantly degraded solar cell performance. Therefore, differences in the impact of the RTA on these structures could also be expected as compared to the lower content solar cells.

6.2.3.1. Effect of annealing on luminescence

The same three annealing temperatures than in the previous series (750, 800 and 850 °C) were employed to anneal different pieces of each of these ~1.0 eV bandgap structures.

PL measurements before and after RTA in the very same sample pieces were employed to test the effect of the different RTA temperatures. The PL parameters extracted from PL GAP peak (ΔI_{GAP} , $\Delta FWHM_{GAP}$ and ΔII_{GAP}) for the three samples and the three temperatures are shown in Figure 6.11. Under the same evaluation criteria that were used in Section 6.2.2.1, 850 °C is the optimum temperature for the *SC-bulk* and *SC-SL 6* samples, though for the *SC-SL 3* the optimum annealing temperature is 800 °C. Nevertheless, it was decided to use the same temperature (850 °C) to anneal the three sample pieces intended to be used to fabricate as solar cells.

Figure 6.11: ΔI_{GAP} (left column), $\Delta \text{FWHM}_{\text{GAP}}$ (center column) and ΔII_{GAP} (right column) obtained by comparing band-to-band-to-band PL peaks of as-grown and RTA samples. Each row corresponds to a different sample (SC-bulk, SC-SL 6 and SC-SL 3). RTA process was performed at 750, 800 and 850 °C; three different pieces of each sample were used, one for each temperature.

Figure 6.12 shows 15 K PL spectra measurements taken over the pieces intended to device processing prior and after the RTA cycle at 850 °C (as-grown and RTA measurements, respectively). PL characteristic values of both GAP peak (II_{GAP} , FWHM_{GAP} and $\text{Blueshift}_{\text{GAP}}$) and N peak (II_{N}) are presented in Table 6.3. Though the PL measurements and the values in the Table are in arbitrary units, both are on the same scale as those in Figure 6.3 and Table 6.1.

Figure 6.12: 15 K PL spectra of samples SC-bulk, SC-SL 6 and SC-SL 3 as-grown (blue lines) and after RTA at 800 °C (red lines).

	Π_{GAP} (arb. units)		FWHM_{GAP} (meV)		$\text{Blueshift}_{\text{GAP}}$ (meV)	Π_{N} (arb units)	
	a-g	RTA	a-g	RTA		a-g	RTA
SC-bulk	0.155	0.647	71	35	147	0.076	0.161
SC-SL 6	0.537	0.820	70	28	52	0.306	0.128
SC-SL 3	0.387	0.180	152	185	0	0.549	0.303

Table 6.3: Quantitative analysis of the PL spectra. Π_{GAP} , FWHM_{GAP} , $\text{Blueshift}_{\text{GAP}}$ and Π_{N} of samples SC-bulk, SC SL 6 and SC SL 3, either as-grown and after RTA.

Only the SC-SL 6 sample has a similar behavior upon annealing treatment to the previous SL samples, showing a similar $\text{Blueshift}_{\text{GAP}}$, a strong increasing of Π_{GAP} and reduction of the FWHM_{GAP} . All this indicates an improved quality after RTA; the intensity of the

sub-bandgap band Π_N is also sharply reduced after annealing. On the other hand, in the *SC-SL 3* sample Π_{GAP} does not increase after annealing but indeed undergoes a non-typical large reduction, and there is no apparent blueshift. Nevertheless, the behavior of the N peak is the expected one, with a reduction of Π_N after RTA. As well as in the previous series, Π_N increases in as-grown samples when the period thickness is reduced (which could be related to the lower homogenous composition when the spatial separation of N and Sb is reduced).

The effect of the RTA on the PL of the *SC-bulk* sample is entirely different from the previous results. The Π_{GAP} strongly increases after annealing, which is the usually observed effect in dilute nitrides materials, but opposite to the behavior of the previous bulk samples (*Bulk 1ML/s* and *Bulk 2ML/s*) of this Thesis. The most noticeably different is an increase of Π_N after RTA that is almost non-existent in the spectrum of the as-grown sample, which is an unexpected result which needs further research.

The different behavior of these “high” N content samples with RTA as compared to the previous “low” content samples could be related to an increasingly important role of localization effects, especially noticeable at low-temperature (as is the case of these PL measurements), and of the non-radiative recombination phenomenon. Both facts could be particularly important in the *SC-bulk* sample, which has more inhomogeneous composition and a larger amount of N-related defects (see Section 6.2.3.1). A substantial reduction of the non-radiative recombination after the RTA in this sample could explain the PL results: in the as-grown sample, recombination in the sub-bandgap states, having very long radiative carrier lifetimes in the range of 200 nanoseconds (information provided by TR-PL measurements), cannot compete with the short non-radiative recombination times linked also to N-induced defects; a reduction of the non-radiative recombination would make possible a weak radiative recombination from the sub-bandgap states and an increase of the Π_N , despite the possible reduction of the number of those states available after RTA.

6.2.3.2. Effect of annealing on structural properties

XRD $\omega - 2\theta$ scans around the (004) GaAs Bragg reflection of the three samples were performed before and after the RTA in the same piece than the PL measurements to verify if the samples undergo any changes in their epitaxial structure after annealing. Figure 6.13 shows the diffractograms corresponding to the samples *SC-bulk* and *SC-SL 6*.

Figure 6.13: $\omega - 2\theta$ scans performed on the SC-bulk and SC-SL 6 samples, both as-grown (solid lines) and after RTA (dashed lines).

The same main peak position is observed before and after annealing for both structures, so again there is not any modification in layer strain caused by RTA. In the SL sample, the SL satellite peaks are also well preserved after RTA, indicating no SL dissolution at the high temperature of 850 °C.

6.2.3.3. Effect of annealing on single-junction solar cell performance

The same pieces of the samples SC-bulk, SC-SL 6 and SC-SL 3 that were optically and structurally analyzed as-grown and after RTA at 850°C in Section 6.2.3.1 and Section 6.2.3.2 were processed as solar cells. In Figure 6.14, room-temperature EQE measurements at 0 V of a representative diode of each RTA sample are shown; the graphs include the EQE measurements at 0 V from as-grown equivalent devices.

The effective bandgap energies of the RTA devices extracted from the peak of the derivative of the EQE spectra at 0 V shown in Figure 6.14 are 1.07 eV for the SC-bulk, 1.11 eV for the SC-SL 6 and 1.12 eV for the SC-SL 3. As expected, there is a blueshift of the bandgap energy in all the RTA samples compared to as-grown devices (70, 40 and 30 meV for SC-bulk, SC-SL 6 and SC-SL 3, respectively) that can be directly observed in the Figure. These values are similar to those obtained in the “low” N content samples series.

However, the 15 K PL of the sample *SC-SL 3* does not experiment a blueshift upon annealing process (Table 6.3). On the other hand, the blueshift in the 15 K PL of the sample *SC-bulk* (147 meV) is much larger than the one observed here at room-temperature. These inconsistencies support the importance of the localization effects in these samples, particularly in the bulk structure: the large blue shift in the 15 K PL spectra would be the addition of the standard blueshift plus the blueshift due to a reduced localization energy as a result of composition homogenization upon RTA.

Figure 6.14: Room temperature EQE at 0 V of one diode of each RTA sample: *SC-bulk*, *SC-SL 6* and *SC-SL 3* (dashed lines) along with the room temperature EQE at 0 V of one diode of each equivalent as-grown samples (solid lines).

In contrast to the previous series (Figure 6.7) in all these devices, the EQE experiences a significant increase after RTA, which points to a reduction of carrier localization, non-radiative recombination or both after annealing. The enhancement of the EQE is larger in the *SC-bulk* sample than in the SLs, which indicates stronger localization effects and non-radiative recombination in the *SC-bulk* sample before annealing, as already discussed.

Figure 6.15 shows the positive voltage region of dark IV curves of RTA and as-grown devices (the latter already shown in Figure 5.8). A reduction of the dark saturation current in annealed diodes can be observed for all the structures.

Figure 6.15: Positive voltage region of the dark IV curves of one diode for each sample, both as-grown and RTA, SC-bulk, SC-SL 6 and SC-SL 3.

The I_0 values of each RTA device, calculated from a fit to the ideal diode equation (Equation (2.1)), are $1.87 \cdot 10^{-4}$ mA/cm² for SC-bulk, $1.26 \cdot 10^{-4}$ mA/cm² for SC-SL 6 and $7.14 \cdot 10^{-5}$ mA/cm² for SC-SL 3. The reduction of I_0 of these samples compared to as-grown samples (values presented in Section 5.2.2.2) is larger than one order of magnitude. The dark saturation current is typically related to the existence of non-radiative recombination: the reduction of the I_0 after RTA is likely due to a reduced non-radiative recombination. The reduction of I_0 is more significant in the case of the SC-bulk, which supports the stronger reduction of non-radiative recombination in this sample (Section 6.2.3.1).

Furthermore, the dark IV curves of RTA devices have a larger slope in the higher voltage region, indicating a reduction of the parasitic series resistance effect that is related to the current flow through the solar cell device. This reduction of series resistance cannot be related to differences in the quality of the metallic contacts or the contact resistance between semiconductor and metal, because the RTA was performed before solar cell processing and the fabrication process was the same for the as-grown and RTA devices. Therefore, the

series resistance reduction has to be attributed to changes in the resistance of the material itself, likely due to the reduced non-radiative recombination and clustering after the annealing process.

Solar characterization under AM1.5G standard conditions was performed on these “high” N content RTA devices. Several solar cells of each RTA sample were tested: 3 for the *SCSL 6 RTA* and *SC-Bulk RTA* samples, and 4 for the *SC-SL 3 RTA* sample. The JV curves of one representative diode of each sample are shown in Figure 6.16, and the average solar cell characteristic values (J_{SC} , V_{OC} , PCE , FF and W_{OC}) with their corresponding errors are in Table 6.4. The values of the equivalent as-grown solar cells are shown in Table 5.2.

Figure 6.16: JV curves under AM1.5G standard illumination of the best diode of each RTA samples: *SC-bulk*, *SC-SL 6* and *SC-SL 3*.

	J_{SC} (mA/cm ²)	V_{OC} (V)	PCE (%)	FF (%)	W_{OC} (V)
<i>SC-bulk RTA</i>	(17±1)	(0.40±0.01)	(4.1±0.2)	(61±1)	(0.67±0.01)
<i>SC-SL 6 RTA</i>	(11±2)	(0.46±0.02)	(2.8±0.4)	(59±4)	(0.65±0.01)
<i>SC-SL 3 RTA</i>	(14±2)	(0.49±0.01)	(4.3±0.5)	(64±2)	(0.63±0.01)

Table 6.4: Average values with its corresponding errors of the solar cell characteristic parameters of several diodes of each RTA sample: *SC-bulk*, *SC-SL 6* and *SC-SL 3*.

As in the “low” N content solar cells, there is a significant enhancement of the V_{OC} . The larger V_{OC} is obtained for the *SC-SL 3 RTA* sample $[(0.49 \pm 0.01) \text{ V}]$, followed by the *SC-SL 6 RTA* $[(0.46 \pm 0.02) \text{ V}]$ and finally the *SC-bulk RTA* $[(0.40 \pm 0.01) \text{ V}]$. The larger V_{OC} in the SL solar cells is not only related with their higher bandgap, as the W_{OC} values are smaller in the SL samples than in the bulk: material quality is better in the SLs, particularly in the SL with 3 nm period, which also has the best FF value $[(64 \pm 2) \text{ \%}]$. On the other hand, the *SC-bulk RTA* has the best J_{SC} $[(17 \pm 1) \text{ mA/cm}^2]$, followed by the *SC-SL 3 RTA* sample $[(14 \pm 2) \text{ mA/cm}^2]$ and finally the *SC-SL 6 RTA* $[(11 \pm 2) \text{ mA/cm}^2]$. In this case, the PCE of the RTA short period SL and the RTA bulk solar cells are comparable $[(4.3 \pm 0.5) \text{ \%}]$ and $[(4.1 \pm 0.2) \text{ \%}]$, respectively].

Therefore, in these “high” N content structures there is not only a strong enhancement of the V_{OC} after RTA (60 %, 53 % and 53% for the *SC-bulk*, *SC-SL 6* and *SC-SL 3* structures, respectively), but also a substantial enhancement of the J_{SC} , contrary to what happened in the lower N content series (see Section 6.2.2.3). In these series the relative J_{SC} increments after annealing are 247 %, 72 % and 47 % for the *SC-bulk*, *SC-SL 6* and *SC-SL 3* structures, respectively. This increment could be due to the stronger reduction of the non-radiative recombination in these “high” N content samples, together with the reduced series resistance (Figure 6.15). Indeed, this reduction of the series resistance was not observed in the “low” N content samples, in which it was already much lower in the as-grown samples (not shown). Remarkably, the increase of the J_{SC} is much larger than in the *GaAs* cell (23 %, presented in Section 5.2.1.2), supporting the idea that the main factor behind this enhancement is related to an improved material quality. There is a strong enhancement of the PCE after RTA in these solar cells. The relative PCE improvements are 503 %, 183 % and 170 % for the *SC-bulk*, *SC-SL 6* and *SC-SL 3* structures, respectively. The much larger improvement in the *SC-bulk* could be related to the worse initial situation regarding material quality and solar cell performance. After the RTA, the performance of the *SC-bulk* becomes close to that of the *SC-SL 3*. However, it is important to notice that the *SC-SL 3* has not been annealed at its optimum RTA temperature, which was determined to be 800 °C instead of 850 °C (see Figure 6.11). A better performance for a *SC-SL 3* solar cell annealed at 800 °C could be expected.

The sub-bandgap radiative states could still play a role in the enhancement of the V_{OC} . Figure 6.17 shows the difference in II_N from the PL spectra and the difference in W_{OC} (ΔW_{OC}) between as-grown and RTA equivalent samples (ΔII_N). Without considering the *SC-bulk* structure because of its negative ΔII_N , a correlation seems to exist between the ΔII_N and the ΔW_{OC} for the SLs cells, which points to a density of the N-related deep radiative

defects reduction after annealing. Nevertheless, results from the bulk sample indicate a much stronger impact of the non-radiative recombination in this “high” N content series.

Figure 6.17: Difference in II_N between RTA and equivalent as-grown samples (right axis) and difference in W_{OC} between RTA and equivalent as-grown samples (left axis) for samples SC-bulk, SC-SL 6 and SC-SL 3.

The W_{OC} values of as-grown and RTA devices of samples SC-bulk, SC-SL 6 and SC-SL 3. (Table 6.2 and Table 6.4) are represented in Figure 6.18 as a function of their respective bandgap energies, together with that of the as-grown and RTA reference GaAs solar cells.

Figure 6.18: W_{OC} as a function of the bandgap energy of samples SC-bulk, SC-SL 6 and SC-SL 3, as-grown (blue dots) and RTA (red triangles). The W_{OC} values of the as-grown and RTA GaAs reference samples are also shown. Dotted lines represent W_{OC} values indicating a material quality similar to that of GaAs.

The W_{OC} values of the as-grown solar cells are far from the *GaAs* value because of the low material quality of these samples. However, the W_{OC} parameter is strongly reduced after RTA, reaching values similar to those of the as-grown *GaAs* solar cell in the case of the *SC-SL 3 RTA*. Nevertheless, the values of all the GaAs(Sb)(N)-based annealed solar cells are well below the W_{OC} of the *GaAs RTA* sample.

6.3. Conclusion

GaAs(Sb)N layers present a broad luminescence band at sub-bandgap energies; the intensity of the emission increases with the N content and decreases with the amount of Sb. In N-containing samples, there is, therefore, a significant density of states within the bandgap related to the existence of N-induced radiative defects, which is reduced after the right RTA process.

On the one hand, the application of the adequate RTA cycle to GaAs(Sb)(N)-based solar cells with ~ 1.15 eV bandgap and relative “low” N and Sb contents improves the V_{OC} significantly. This improvement is related to reduced radiative recombination at sub-bandgap states. Remarkably, the W_{OC} of the annealed GaAs(Sb)(N)-based solar cells is equivalent or even lower than that of a reference GaAs cell, which indicates high material quality. Nevertheless, the *PCE* is not improved after RTA due to a reduction of the J_{SC} .

On the other hand, the application of the adequate RTA cycle to GaAs(Sb)(N)-based solar cells with ~ 1.0 eV bandgap and relative “high” N and Sb contents improves both the V_{OC} and the J_{SC} significantly. As a result of this, relative improvements of the *PCE* as high as 503 % are obtained.

The differences in the effect of RTA on the two series of samples are likely due to the much stronger effect of non-radiative recombination and carrier localization in the “high” N content structures. This stronger effect would also reduce the relative impact of the sub-bandgap radiative states on the V_{OC} , which could play a critical role in the “low” N content samples in which non-radiative recombination is weaker than in “high” N content samples.

The large increase of the J_{SC} after RTA in 1.0 eV samples is particularly relevant since it could help to provide current matching when integrated in a MJSC. Therefore, these results represent an important step towards the integration of GaAs_{1-x}Sb_x/GaAs_{1-y}N_y SLs in GaAs/Ge-based MJSC.

7. Conclusions

Strain-balanced type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs have been proved to be a very promising structure to be implemented in high efficiency MJSCs as the required layer with 1.0–1.15 eV bandgap and lattice-matched to GaAs/Ge. To the best of our knowledge, this kind of (pseudo)material and its potential application on photovoltaics have been exhaustively examined for the first time during this Thesis work. The partial achievements and conclusions obtained in the Thesis are listed below.

Material growth and properties

- Type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs can overcome the growth problems present in the quaternary $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ alloy (that affect both thick layers and type-I $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$ SLs) because of the spatial separation of N and Sb atoms during epitaxial growth. Therefore, type-II SLs give rise to a better composition and lattice-matching control, as well as to an improved crystal quality and interface abruptness. Remarkably, this is obtained by using half the amount of N and Sb than in the bulk counterparts.
- Although the N content profile in the SLs is accurately controlled, the type-II SL nominal structure is not perfectly preserved because of Sb segregation. This effect is mitigated for longer period thicknesses.
- Accurate control of SL period thickness has been demonstrated even for thin periods in the range of 3 nm, as well as effective bandgap tunability through period thickness due to quantum confinement.
- The type-II SLs have longer radiative lifetimes (particularly helpful for to avoid radiative recombination before extraction in solar cells) than equivalent bulk and type-I SLs. Carrier lifetime is also tunable through period thickness, a unique property of these structures which is not possible in type-I SLs.

- Carrier transport dynamics are also affected by period thickness: the transport regime changes from quasi-ballistic in short period SLs to sequential tunneling combined with thermionic escape in long period SLs. This change in the carrier mechanism causes a drop in the carrier extraction efficiency for thick periods. In any case, extraction efficiency is better in type-II SLs than in the equivalent type-I structures due to the longer radiative lifetimes.

Single-junction solar cell performance

- SL solar cells with ~ 1.15 eV bandgap show inefficient carrier extraction for periods of 12 nm, while smaller periods of 6 nm provide complete carrier collection at 0 V; this is due to the change in the transport regime predicted by the model.
- This makes SL solar cells with 12 nm period very inefficient, while the *PCE* of the 6 nm SL solar cell is close to that of the bulk counterparts. For the “low” N and Sb contents required in the 1.15 eV structures, the SL approach is not advantageous in terms of solar cell *PCE*.
- For the higher N and Sb contents required in the 1.0 eV structures, the SL approach is advantageous in terms of solar cell *PCE*. Indeed, 3 nm period SL solar cells show an enhanced *PCE* of 134 % over the equivalent bulk devices.
- Solar cells with ~ 1.0 eV bandgap show degraded performance due to the increased N content. The carrier extraction efficiency at 0 V is far from 100 % even for thin periods of 3 nm, which is likely due to strong non-radiative recombination and carrier localization effects.

Effect of rapid thermal annealing

- There is a significant density of states within the bandgap in N-containing samples, which is related to the existence of N-induced radiative defects.
- The application of an adequate RTA process reduces the density of sub-bandgap states and improves the crystalline quality of the alloy; in particular, the Sb composition becomes more homogeneous after RTA.

- In solar cells with ~ 1.15 eV bandgap and relative “low” N and Sb contents RTA improves the V_{OC} significantly; in solar cells with ~ 1.0 eV bandgap and relatively “high” N and Sb contents not only the V_{OC} but also the J_{SC} strongly increase after RTA, especially in the bulk solar cell, in which non-radiative recombination and carrier localization effects are initially stronger.
- Remarkably, the W_{OC} of the annealed ~ 1.15 eV GaAs(Sb)(N)-based solar cells is equivalent or even lower than that of a reference GaAs cell, which indicates high material quality.
- The significant increase of J_{SC} after RTA in 1.0 eV samples is particularly relevant since it could help to provide current matching when integrated in a MJSC.

8. Future work

8.1. Improvements in superlattice design

The results obtained during this Thesis demonstrate that strain-balanced type-II $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SL structures with thin periods have a great potential to be successfully implemented as 1.0–1.15 eV layer in MJSCs. Despite the promising results, their potential has yet to be fully realized. The continuation of the research would allow optimizing the SLs structures and fully exploit their advantages. Three consecutive SL design strategies are planned:

8.1.1. Accurate superlattice interface control

A very accurate control over the SL structure and interfaces is mandatory for the growth of high-quality SLs with period thickness in the range of 3 nm.

According to EDX results shown in Section 4.2.1.1 and Section 4.2.2.1, this SL structure presents strong Sb segregation. Therefore, SLs do not have a perfect $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ square-like profile with abrupt interfaces, but Sb segregates into the $\text{GaAs}_{1-y}\text{N}_y$ layers, so $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ structures with a spiky Sb profile distribution are obtained, which modifies the band structure. This deviation of composition profiles from expected rectangular profiles caused by the Sb surface segregation can have a significant influence on the optical properties of semiconductor QWs and SLs [240]. The concomitant presence of N and Sb during growth modifies N incorporation. Moreover, Sb incorporation in the $\text{GaAs}_{1-x}\text{Sb}_x$ layers is very gradual and sensitive to the Sb accumulation on the growth surface before the $\text{GaAs}_{1-x}\text{Sb}_x$ layer growth starts.

Different growth strategies can be carried out to improve the type-II SL composition profiles and control the interfaces to the ML level:

- (1) Sb-flux on the growth surface before the $\text{GaAs}_{1-x}\text{Sb}_x$ layer growth to assure an accumulation of Sb which would avoid gradual Sb incorporation in the layer [241].

- (2) Growth interruption under As-flux and increased temperature after $\text{GaAs}_{1-x}\text{Sb}_x$ layer growth to eliminate the Sb-floating layer before $\text{GaAs}_{1-y}\text{N}_y$ growth, which would avoid the segregation of Sb to the $\text{GaAs}_{1-y}\text{N}_y$ layer as well as the undesired modification of the N content in the layer [213].
- (3) Combination of both strategies [242].

8.1.2. Asymmetric period superlattices

Until now type-II SL structures with $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-y}\text{N}_y$ and layers of identical thickness have been produced. However, the thicknesses of $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-y}\text{N}_y$ layers can be varied independently, which, because of the unique properties of this material, allow the independent control of electron and hole electronic coupling and transport in the structure. The quantum kinetic NEGF calculations shown in Section 4.2.2.4 predict enhanced photovoltaic performance for certain asymmetric configurations with thinner $\text{GaAs}_{1-x}\text{Sb}_x$ and thicker $\text{GaAs}_{1-y}\text{N}_y$ layers [243]. Therefore, this asymmetric SLs should be grown to take advantage of the approach fully. For each of the two proposed research lines, it is necessary to cover the whole process:

- (1) MBE growth of novel $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SL designed with the previously mentioned interface control strategies and asymmetric periods.
- (2) Exhaustive optical and structural characterization of the new SLs and careful determination of the real compositional profiles by a combination of modeling and advanced EDX studies.
- (3) Device fabrication and characterization: correlation of the optical and structural properties at the atomic scale of the nanostructures with their behavior as solar cell devices.

8.1.3. Optimization of superlattice thickness

All of the solar cells studied in this Thesis have a total active layer thickness of 816 nm. On the one hand, a thicker absorbing layer means the increasing of the total absorption volume and the amount of photogenerated carriers, which could lead to an enhancement of J_{SC} . Having a high J_{SC} is a critical issue to achieve current matching when the sub-cell is inserted in a MJSC. On the other hand, the photocarriers generated in the intrinsic layer are collected with the aid of the built-in electric generated by the p-i-n structure. The intensity

of such electric field decreases with layer thickness, so making the intrinsic layer thicker could give rise to carrier recombination instead of efficient carrier extraction.

However, the beneficial effect of increasing the absorbing layer in dilute nitride p-i-n solar cells has been already demonstrated. EQE and J_{SC} of $GaAs_{1-x-y}Sb_xN_y$ and $Ga_{1-x}In_xAs_{1-y}N_y:Sb$ solar cells have been shown to increase with the active layer thickness from 0.6 μm to 1 μm in as-grown structures [78,238]. The effect is also noticeable for larger thicknesses in annealed solar cells: though increasing the $Ga_{1-x}In_xAs_{1-y}N_y:Sb$ layer thickness from 1 μm to 3 μm results in as-grown solar cells in a reduction of the J_{SC} due to recombination losses, after RTA the J_{SC} increases for the 2 and 3 μm solar cells compared to the 1 μm one because of the improved field-assisted carrier collection [56]. Then, the solar cell structures employed in this Thesis can reach higher J_{SC} values increasing their layer thickness. In particular, the growth and fabrication of solar cells with thick intrinsic layers with short period thickness type-II SLs, where minibands extended across the whole structure assists the carrier extraction, could be especially attractive.

8.2. Growth of multi-junction solar cells

8.2.1. Growth of optimized superlattice single-junction cells

J_{SC} values and overall solar cell performance obtained in this Thesis would be significantly improved by a proper solar cell design since the solar cell structure of the samples of this Thesis is completely un-optimized (see Section 3.1.2 and Section 3.3). Different optimization strategies could be carried out:

- (1) Analysis of residual doping by Capacitance-Voltage (CV) measurements and study of defects by Deep Level-Transit Spectroscopy (DLTS) should be carried out with the aim of improving the doping profile, designing correctly the intrinsic zone of the solar cell and becoming aware about the existence and the role played by defects in the electrical and optical properties of the cells.
- (2) Increment of the solar cells surface area, which would lead to increment of the photon absorption and therefore of the J_{SC} . Also, this would reduce the P/A ratio. Solar cells can undergo undesired perimeter recombination losses if their P/A ratio is high (see Section 3.3). Currently, our fabricated solar cell has a P/A value of 200 cm^{-1} ; according to a model developed elsewhere [185], the V_{OC} of a GaAs solar cell drops by 4 % and the efficiency by 12 % for a cell with the same diameter than ours compared to a large area solar cell.

- (3) Use of window layer: the addition of a window layer on top of the absorbing layer prevents electron recombination in the front surface of the cell, which profoundly affects the J_{SC} . In GaAs-based solar cells, one of the most common window layer consists of an AlGaAs layer [146,244].
- (4) Use of BSF layer: this layer contributes to high V_{OC} by introducing a barrier to minority carrier flow to the rear surface, without increasing the R_S . As the window layer, in GaAs-based solar cells, the BSF layer usually consists of an AlGaAs layer at the back of the cell [148].

Therefore, the growth of high-quality AlGaAs by MBE is required for obtaining both window and BSF layers. Preliminary studies have been already performed to calibrate Al incorporation on GaAs and to correlate Al content and layer thickness with the optical and structural properties of the layers.

- (5) Use of a p^{++} contact layer on top of the 50 nm-thick p^+ emitter epitaxial layer could reduce contact resistance.

8.2.2. Growth of GaAs-superlattice tandem cell

In this Thesis, solar cell study has been limited to single-junction solar cells. A further step towards the effective integration of type-II $GaAs_{1-x}Sb_x/GaAs_{1-y}N_y$ SLs as a sub-cell in MJSC would consist on the growth of a monolithic tandem solar cell composed of a 1.46 eV GaAs layer grown on top of a 1.0–1.15 eV SL. The electrical connection between both sub-cells would be provided by a tunnel junction, which consists of a conductive, optically transparent semiconductor layer that increases the overall device efficiency. In our case, the tunnel junction would consist of a highly doped (Al)(Ga)As thin layer deposited during MBE growth.

8.3. $GaAs_{1-y}N_y/Al_yGa_{1-y}As_{1-x}Sb_x$ SLs for intermediate band solar cells

The third-generation solar cells with the highest degree of development are the MJSCs, which are already a commercially available technology (See Section 1.2). The intermediate band solar cell (IBSC) is the second strategy more intensively investigated today, although it is still at the demonstration level. IBSC was proposed as a means of enhancing the conversion efficiency of single-gap solar cells [245]. In this device, the presence of an

intermediate band (IB) between the CB and VB bands allows electrons to be promoted either directly to the conduction band via a single high-energy photon, or via the IB with two low-energy photons. Therefore, the cell can also capture the solar energy from sub-bandgap low-energy photons, while it has the voltage of the highest energy bandgap (if the bands are thermally isolated). The theoretical efficiency of an ideal IBSC device is predicted to approach 45 % and 63 % under 1 Sun and maximum sunlight concentration, respectively [245]. IBSC, as well as MJSC, are typically based on epitaxial semiconductor (nano)structures, thereby precise strain and band structure engineering are of key importance to its achievement.

The main approaches to IBSC are based on multiple quantum dots (QDs) layers inserted in the active region of the solar cell [246]. Indeed, so far the two operating principles of an IBSC (the production of an extra sub-bandgap photocurrent and the preservation of the output voltage) have only been demonstrated in simple InAs/GaAs QD-IBSCs [247].

Apart from the QDs strategies, QWs are also being investigated to produce IBSCs [248]. The type-II structures developed in this Thesis could be, with a slight modification, interesting for this application. They can provide confined states for electrons with long radiative lifetimes, as required for IBSCs. The considerable confinement potential required could be achieved by adding Al to the $\text{GaAs}_{1-x}\text{Sb}_x$ layer.

Indeed, $\text{GaAs}_{1-y}\text{N}_y/\text{Al}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{Sb}_x$ QWs are very promising to further advance towards efficient IBSC. They provide the ideal IB design in a two-dimensional structure: a type-II or flat VB profile and a very high potential barrier at the CB. Moreover, they can be grown lattice-matched to GaAs. A potential advantage over QD-IBSC is the larger absorption volume and density of states of the QW or SL compared to the QDs [248]. Nevertheless, the fact that the density of states is non-zero between the IB and the CB could be a significant drawback for the realization of an IBSC.

8.4. Hydrogenation of GaAs(Sb)(N)-based materials

Hydrogenation is a process that can be performed in dilute nitride materials [249,250], like $\text{GaAs}_{1-y}\text{N}_y$. The process consists of the irradiation of material surface with a low energy (~ 100 eV) H-ion flux, in such a way that the H is incorporated in the material in the form of different N-nH complexes (N-2H and N-3H) [251,252]. H can be easily placed inside the crystal because the N-H bond is strong. The introduction of H renormalizes the charge distribution around the N atoms, neutralizing the effect caused by N so the original GaAs

properties can be recovered [253]. The N-2H complex is responsible for the restoration of the bandgap to the value of N-free GaAs, while N-3H influences the strain in the material.

Moreover, the recovery of the effect of N is achievable through a thermal annealing process. The N-3H complex disappears above 250 °C, and N-2H complex disappears above 330 °C [251]. The hydrogenation process has a localized impact (it is only effective in the area where the H ion flux impinges and has limited penetration). The created N-nH complexes can also be removed at a local scale, for example by laser irradiation.

That versatility achieved combining hydrogenation and recovering process would allow the creation of nanostructured materials with different properties in different areas, according to a desired pattern [252,254,255]. Hence, carrying out such a procedure in $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ type-II SLs could give rise to a metamaterial with interesting properties to explore.

Though the hydrogenation effect in $\text{GaAs}_{1-y}\text{N}_y$ is well known, the effect of hydrogenation on $\text{GaAs}_{1-x}\text{Sb}_x$ is unknown up to now. Sb is a big atom, so a weaker tendency to create Sb-H bonds than N-H bonds can be expected. Regardless of the hydrogenation effect on $\text{GaAs}_{1-x}\text{Sb}_x$, the hydrogenation of $\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$ SLs could be interesting in any case.

This project has already started, in collaboration with the Photonics and Semiconductor Nanophysics Group of Prof. Paul Koenraad, from Eindhoven University of Technology. This laboratory counts on a unique technology, cross-sectional scanning tunneling microscopy (X-STM) that in this case is determinant to directly study the presence of N-nH complexes at the atomic scale as well as the exact distribution of N and Sb inside the samples.

To date, some advances have been made. The effect of hydrogenation in $\text{GaAs}_{1-y}\text{N}_y$ QWs has been analyzed by X-STM. Three different features have been observed, one of them related to the presence of N on the sample surface, and the other two, which have never been seen before on non-passivated N:GaAs, related to the presence of N-nH complexes. Furthermore, a $\text{GaAs}_{1-y}\text{N}_y$ thick layer and a $\text{GaAs}_{1-x}\text{Sb}_x$ thick layer have been already analyzed to study the effect of the combination of hydrogenation and subsequently annealing. To the best of our knowledge, the effect of hydrogenation on $\text{GaAs}_{1-x}\text{Sb}_x$ has been studied for the first time. PL and XRD measurements were performed on both samples. Then, a hydrogenation process has been carried out introducing the samples in an inductively induced plasma (ICP) instrument working with at a RF power of 6 W. An H_2 -rich plasma was generated using an H_2 flux that was ionized with an ICP power of 100 W

at a pressure of 30 mTorr. The samples were exposed during one hour to the created $\sim 4 \cdot 10^{14}$ ions cm^{-2} seconds $^{-1}$ flux. Finally, PL and XRD are measured again. The expected effect of an effective hydrogenation is a reduction in the PL peak intensity corresponding to $\text{GaAs}_{1-y}\text{N}_y$ and an increase in the PL peak intensity corresponding to GaAs. In XRD, it is expected that in addition to the GaAs and $\text{GaAs}_{1-y}\text{N}_y$ layer peaks, a secondary peak appears in the strained region of the diffractogram associated with H-N pairs [250,251,253]. These effects have been observed in the $\text{GaAs}_{1-y}\text{N}_y$ bulk samples, but no change has been observed up to now in $\text{GaAs}_{1-x}\text{Sb}_x$.

These preliminary results have already been presented at a conference (see List of publications and conference Section). Further efforts dedicated to carry out hydrogenation process on more $\text{GaAs}_{1-x}\text{Sb}_x$ and $\text{GaAs}_{1-y}\text{N}_y$ samples and especially on type-II SLs, and analysis through X-STM, are required to continue this line of investigation.

Appendix A. Growth calibration

A.1. N flux: GaAs_{1-y}N_y thick layers

Six different samples consisting of a 200 nm thick GaAs_{1-y}N_y layer deposited on top of a 250 nm thick GaAs buffer layer were grown. The samples were grown under different N fluxes, so different N contents are expected. The active N flux is proportional to the monitored OED, which depends on the RF power of the plasma source, and on the N₂ flow provided which in our case is always set up to 0.1 sccm (see Section 3.1). Five of the samples were grown at the usual 1ML/s (samples *GaAsN-1*, *GaAsN-2*, *GaAsN-3*, *GaAsN-4* and *GaAsN-5*), with OED values during growth between 585 and 1260 mV, and the other one (sample *GaAsN-6*) was grown at a different growth rate (2 ML/s) with an OED value of 633 mV. The samples are listed in Table A.1, and their complete set of active layer growth parameters are described in Table B.4, Appendix B.

The objective of this series of samples is to check that the N incorporation is effectively proportional to the OED, which would allow calibrating the N incorporation for further quaternary growth; to check the effect that the N incorporation has in the bandgap energies and lattice constants of the samples, and also to check the effect of the growth rate on the N incorporation.

The samples were analyzed by XRD and PL techniques. The $\omega - 2\theta$ scans of each sample, along with the fitted XRD simulations, are shown in Figure A. 1. All the XRD diffractograms consist of the GaAs substrate peak at 33.0239° and a main peak related to the GaAs_{1-y}N_y layer. A layer thickness of 200 nm is used in the simulations, which determine good adjustment to the nominal thickness, assuring the right adjustment of the growth rate during the growth process. The simulations also allow extracting the N content introduced in the active layer with reasonable precision due to the reduced broadness of the main XRD peak. The effective N content ranges from 0.37 % to 1.10 %; the precise values of each sample are presented in Table A.1. It has been assumed that the N-containing layers have been pseudomorphically grown over the GaAs buffer layer, which has been demonstrated through TEM measurement in sample *GaAsN-1* as well as in all other GaAs(Sb)(N) samples

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grown by us and analyzed by TEM, including quaternary $\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y$ samples with active layer thickness up to 750 nm [256].

Figure A. 1: $\omega - 2\theta$ scans (bright lines) and the fitted simulations (faded lines) of the samples GaAsN-1, GaAsN-2, GaAsN-3, GaAsN-4, GaAsN-5 and GaAsN-6.

The measured XRD diffractograms of these six samples are shown all together in Figure A.2 a). The N contents extracted from the XRD simulations versus the corresponding OED values are represented in Figure A.2 b). Points corresponding to the 1ML/s samples are well distributed along a straight line with zero intercept; then, the N incorporation in the $\text{GaAs}_{1-y}\text{N}_y$ layers can be accurately controlled by OED monitoring. On the other hand, the N incorporation in the 2ML/s growth rate sample is half than the value expected from the 1ML/s calibration line: therefore, the N incorporated in the epitaxial film is inversely proportional to the growth rate. The differences in the N content between different samples are proportional to the separation between the corresponding $\text{GaAs}_{1-y}\text{N}_y$ peaks of the XRD scans.

Figure A.2: a) $\omega - 2\theta$ scans of the samples GaAsN-1, GaAsN-2, GaAsN-3, GaAsN-4, GaAsN-5 and GaAsN-6. b) Amount of N incorporated in the different $\text{GaAs}_{1-y}\text{N}_y$ layers (measured by XRD) as a function of the OED of the plasma during the growth process.

The PL spectra of the $\text{GaAs}_{1-y}\text{N}_y$ samples appear in Figure A.3 a). The PL peak energy position is shifted toward lower energies as the amount of N in the sample increases. Figure A.3 b) shows the N contents calculated by XRD simulation of each sample versus the energy of the PL peak. In this range of N contents (0.37–1.10 % N) bandgap energies of the samples as a function of the N content are approximately arranged along a straight line. A linear fit to the data indicates that the bandgap energy decreases ~ 163 meV/% N in this range of contents; the total bandgap energy reduction extracted from the PL spectra is 122 meV. The Figure also indicates that for N contents below 0.4 %, bandgap reduction must be stronger: PL peak energy of GaAs at low-temperature is located at 1510 meV, so a higher slope is expected in that region. These experimental results agree with the bandgap energy reduction

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predicted by the DBAC model [68,69]: the model predicts a total bandgap energy reduction of ~ 110 meV for the range of N contents between ~ 0.4 – 1.1 %, and it also predicts a larger bandgap reduction for N contents below ~ 0.5 %.

Figure A.3: a) 15 K PL spectra of the samples GaAsN-1, GaAsN-2, GaAsN-3, GaAsN-4, GaAsN-5 and GaAsN-6. b) Energy position of the PL peaks of the different $GaAs_{1-y}N_y$ layers (measured by XRD) as a function of the amount of N incorporated in each sample.

The growth rates and the OED values during the growth of each sample, along with the N contents obtained from the XRD simulations and the energies of the PL peak obtained from the PL spectra (PL_{PEAK}) are shown in Table A.1.

	Growth rate (ML/s)	OED (mV)	% N (XRD)	PL_{PEAK} (meV)
<i>GaAsN-1</i>	1 ML/s	1260	1.10	1238
<i>GaAsN-2</i>	1 ML/s	1080	0.90	1278
<i>GaAsN-3</i>	1 ML/s	944	0.85	1292
<i>GaAsN-4</i>	1 ML/s	655	0.60	1308
<i>GaAsN-5</i>	1 ML/s	585	0.53	1348
<i>GaAsN-6</i>	2 ML/s	633	0.37	1360

Table A.1: Growth rate, OED, N content extracted from XRD and PL_{PEAK} energy position of the $GaAs_{1-y}N_y$ thick layer samples.

A.2. Sb flux: $\text{GaAs}_{1-x}\text{Sb}_x$ thick layers

Four different samples with 200 nm thick $\text{GaAs}_{1-x}\text{Sb}_x$ active layers deposited over 250 nm thick GaAs buffer layers were grown for the same purpose as the $\text{GaAs}_{1-y}\text{N}_y$ series. In this case, the Sb incorporation is expected to be proportional to BEP of the Sb flux, measured through a Bayard Alpert ion gauge, which in turn is proportional to the temperature of the Sb cell (see Section 3.1). Three of the samples were grown at 1ML/s (samples *GaAsSb-1*, *GaAsSb-2*, *GaAsSb-3*) with BEP Sb from $8.00 \cdot 10^{-9}$ to $1.87 \cdot 10^{-7}$ Torr, and the other one at 2ML/s (sample *GaAsSb-4*) with BEP Sb of $1.70 \cdot 10^{-7}$ Torr. The samples are listed in Table A.2, and the growth parameters of their active layers are described in Table B.4, Appendix B.

The samples were analyzed by XRD and PL. The $\omega - 2\theta$ scans of each sample, consisting of the substrate and the $\text{GaAs}_{1-x}\text{Sb}_x$ layer peaks, along with the XRD simulation that best fitted the experimental measurements are shown in Figure A. 4

Figure A. 4: $\omega - 2\theta$ scans (bright lines) and the fitted simulations (faded lines) of the samples *GaAsSb-1*, *GaAsSb-2*, *GaAsSb-3* and *GaAsSb-4*.

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The simulations confirm again the good agreement of the active layer thickness to the nominal one, indicating the precision of the growth rate. The Sb contents of the layers are also extracted from the performed simulations, assuming pseudomorphic growth again, and range from 1.2 to 7.1 % (the Sb content are detailed in Table A.2).

The measured XRD diffractograms of these $\text{GaAs}_{1-x}\text{Sb}_x$ samples are shown all together in Figure A. 5 a). Figure A. 5 b) shows the Sb contents extracted from the XRD simulations versus the corresponding BEP measured for the Sb fluxes. In this case, 1ML/s samples are also distributed along a straight line, confirming the relationship between the Sb flux and the Sb incorporation. Sb incorporation for 2ML/s growth rate sample is approximately half of the corresponding incorporation for 1ML/s, meaning that incorporation of Sb is also inversely proportional to the growth rate in this range of Sb fluxes. The differences in the calculated Sb contents is proportional to the separation of the Sb-layer peaks of the different XRD scans.

Figure A. 5: a) $\omega - 2\theta$ scans of the samples GaAsSb-1, GaAsSb-2, GaAsSb-3, GaAsSb-4. b) Amount of Sb incorporated in the different $\text{GaAs}_{1-x}\text{Sb}_x$ layers (measured by XRD) as a function of the Sb BEP measured for the Sb fluxes.

The PL spectra of the samples appear in Figure A. 6. a). The PL peak energy position is progressively reduced as the Sb content increases. Figure A. 6. b) shows the Sb contents extracted from XRD of each sample versus the PL_{PEAK} from the PL spectra. In this range of Sb contents (1.2–7.1 % Sb), the points are distributed along a straight line. A linear fit indicates that the bandgap energy decreases in this range $\sim 24 \text{ meV}/\% \text{ Sb}$ (the total bandgap

energy reduction in the full range is 98 meV). It can be noticed that incorporation would follow approximately the same linear trend for Sb contents lower than 1.2 %. That experimental results match with calculated bandgap reduction by DBAC model in [66], which predicts a bandgap energy reduction of ~ 100 meV for the range of Sb contents between ~ 1 –7 %, and a completely linear trend.

Figure A. 6: a) 15 K PL spectra of the samples GaAsSb-1, GaAsSb-2, GaAsSb-3 and GaAsSb-4. b) Energy position of the PL peaks of the different GaAs_{1-x}Sb_x layers (measured by XRD) as a function of the amount of Sb incorporated in each sample.

Surprisingly, the PL peak intensity of the Sb-containing samples shows a rising trend as the Sb content increases, being significantly higher for the sample with 7.1 % Sb. Though there is literature demonstrating intense PL peaks from GaAs_{1-x}Sb_x QW with low Sb contents, there is almost no literature showing PL of GaAs_{1-x}Sb_x bulk layers with Sb contents lower than ~ 5 %, as far as we know; the PL studies performed in bulk GaAs_{1-x}Sb_x are over samples with Sb contents higher than 6 % [229,230]. Different factors could have an influence on the low PL intensity of these GaAs_{1-x}Sb_x samples. For example, the growth temperature (470 °C) of all the samples of this Thesis, including the GaAs_{1-x}Sb_x ones, is optimized for the growth of N-containing samples (see Section 3.1); however, the GaAs_{1-x}Sb_x is usually grown at temperatures higher than 500 °C [229,230,257]. On the other hand, it has been reported that the PL emission from GaAs_{1-x}Sb_x mainly comes from localized states [230]. It could happen that for very low Sb contents, there is still almost no composition inhomogeneities, and therefore not many localized states. In this case, the

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observed PL emission would come from band-to-band transitions, which are typically weaker than those coming from localized states.

The growth rates and the Sb BEP values of each sample, along with the Sb content obtained from XRD simulations and PL_{PEAK} obtained from PL are shown in Table A.2.

	Growth rate (ML/s)	BEP Sb (Torr)	% Sb (XRD)	PL_{PEAK} (meV)
<i>GaAsSb-1</i>	1 ML/s	$1.85 \cdot 10^{-7}$	7.1	1351
<i>GaAsSb-2</i>	1 ML/s	$8.40 \cdot 10^{-8}$	2.2	1476
<i>GaAsSb-3</i>	1 ML/s	$8.00 \cdot 10^{-9}$	1.2	1494
<i>GaAsSb-4</i>	2 ML/s	$1.70 \cdot 10^{-7}$	3.8	1449

Table A.2: Growth rate, BEP, Sb content extracted from XRD and PL_{PEAK} energy position of the $GaAs_{1-x}Sb_x$ thick layer samples

Appendix B. Growth parameters of active layers of all samples in the Thesis

Thickness (nm)	Growth rate (ML/s)	Number of periods	OED (mV)	RF power (W)	BEP Sb (Torr)	T Sb (°C)	BEP As ₄ (Torr)
<i>SL-Sb</i>	1	18	--	--	$1.36 \cdot 10^{-7}$	345	$1.8 \cdot 10^{-5}$
<i>SL-N</i>	1	18	1480	65	--	--	$1.8 \cdot 10^{-5}$
<i>SL-I</i>	1	18	1460	66	$1.37 \cdot 10^{-7}$	346	$1.9 \cdot 10^{-5}$
<i>SL-II</i>	1	18	1480	68	$1.38 \cdot 10^{-7}$	342	$1.9 \cdot 10^{-5}$
<i>bulk</i>	1	--	1470	66	$1.37 \cdot 10^{-7}$	346	$1.9 \cdot 10^{-5}$
<i>SL-20</i>	1	12	1480	65	$1.37 \cdot 10^{-7}$	343	$1.8 \cdot 10^{-5}$
<i>SL-12</i>	1	18	1480	68	$1.38 \cdot 10^{-7}$	342	$1.9 \cdot 10^{-5}$
<i>SL-6</i>	1	36	1480	65	$1.37 \cdot 10^{-7}$	343	$1.8 \cdot 10^{-5}$
<i>SL-3</i>	1	72	1480	64	$1.40 \cdot 10^{-7}$	344	$1.8 \cdot 10^{-5}$

Table B.1: Description of growth parameters of samples appearing in Chapter 4.

	Thickness (nm)	Growth rate (ML/s)	Number of periods	OED (mV)	RF power (W)	BEP Sb (Torr)	T Sb (°C)	BEP As ₄ (Torr)
<i>SL-I 12</i>	816	1	68	2240	98	$2.03 \cdot 10^{-7}$	359	$1.9 \cdot 10^{-5}$
<i>SL-II 12</i>	816	1	68	2260	98	$2.01 \cdot 10^{-7}$	356	$1.8 \cdot 10^{-5}$
<i>SL-II 6</i>	816	1	136	2250	96	$2.03 \cdot 10^{-7}$	387	$1.8 \cdot 10^{-5}$
<i>Bulk 1ML/s</i>	816	1	--	1530	69	$2.57 \cdot 10^{-7}$	369	$1.7 \cdot 10^{-5}$
<i>Bulk 2ML/s</i>	816	2	--	3050	132	$2.50 \cdot 10^{-7}$	372	$1.8 \cdot 10^{-5}$
<i>GaAs</i>	816	1	--	--	--	--	--	$1.8 \cdot 10^{-5}$
<i>SC-SL 6</i>	816	1	136	2580	117	$9.3 \cdot 10^{-8}$	313	$1.6 \cdot 10^{-5}$
<i>SC-SL 3</i>	816	1	272	2680	129	$1.07 \cdot 10^{-7}$	314	$1.5 \cdot 10^{-5}$
<i>SC-bulk</i>	816	1	--	2260	118	$8.6 \cdot 10^{-8}$	310	$1.5 \cdot 10^{-5}$

Table B.2: Description of growth parameters of samples appearing in Chapter 5.

Thickness (nm)	Growth rate (ML/s)	Number of periods	OED (mV)	RF power (W)	BEP Sb (Torr)	T Sb (°C)	BEP As ₄ (Torr)
<i>GaAsSb</i>	1	--	--	--	$8.4 \cdot 10^{-8}$	330	$1.9 \cdot 10^{-5}$
<i>GaAsSbN</i>	1	--	1286	60	$1.12 \cdot 10^{-7}$	335	$1.6 \cdot 10^{-5}$
<i>GaAsN (0.4 % N)</i>	2	--	633	42	--	--	--
<i>GaAsN (0.6 % N)</i>	1	--	655	45	--	--	--
<i>GaAsN (0.9 % N)</i>	1	--	1080	53	--	--	--
<i>GaAsN (1.1 % N)</i>	1	--	1260	60	--	--	--
<i>GaAsSbN (3.4 % Sb)</i>	2	--	3010	132	$1.57 \cdot 10^{-7}$	345	$1.8 \cdot 10^{-5}$
<i>GaAsSbN (3.7 % Sb)</i>	2	--	2930	133	$1.76 \cdot 10^{-7}$	349	$1.9 \cdot 10^{-5}$
<i>GaAsSbN (5.9 % Sb)</i>	2	--	3000	132	$2.60 \cdot 10^{-7}$	361	$1.9 \cdot 10^{-5}$
<i>GaAsSbN (9.6 % Sb)</i>	2	--	3010	132	$3.39 \cdot 10^{-7}$	364	$1.8 \cdot 10^{-5}$

Table B.3: Description of growth parameters of samples appearing in Chapter 6.

	Thickness (nm)	Growth rate (ML/s)	Number of periods	OED (mV)	RF power (W)	BEP Sb (Torr)	T Sb (°C)	BEP As ₄ (Torr)
<i>GaAsN-1</i>	200	1	--	1260	60	--	--	--
<i>GaAsN-2</i>	200	1	--	1080	53	--	--	--
<i>GaAsN-3</i>	200	1	--	944	50	--	--	--
<i>GaAsN-4</i>	200	1	--	655	45	--	--	--
<i>GaAsN-5</i>	200	1	--	585	42	--	--	--
<i>GaAsN-6</i>	200	2	--	633	42	--	--	--
<i>GaAsSb-1</i>	200	1	--	--	--	$1.85 \cdot 10^{-7}$	350	$1.6 \cdot 10^{-5}$
<i>GaAsSb-2</i>	200	1	--	--	--	$8.4 \cdot 10^{-8}$	330	$1.9 \cdot 10^{-5}$
<i>GaAsSb-3</i>	200	1	--	--	--	$4.8 \cdot 10^{-8}$	315	$1.7 \cdot 10^{-5}$
<i>GaAsSb-4</i>	200	2	--	--	--	$1.90 \cdot 10^{-7}$	347	$1.6 \cdot 10^{-5}$

Table B.4: Description of growth parameters of samples appearing in Appendix A.

Appendix C. Theoretical models

C.1. Sb segregation model

A model for the Sb segregation is used to fit the distribution of Sb measured over several periods in type-II ($\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$) SLs, which leads to the Sb concentration profiles that are presented in Figure 4.9.

These simulations have been performed by the research group of Professor David González from Departamento de Ciencias de los Materiales e IM y QI at Universidad de Cádiz. The Sb segregation model employs the fluid three-layer exchange mechanism [258,259], which establishes that during the growth of one ML, the Sb/As exchange process involves three layers: the growth front and the two first buried layers.

The evolution of the fraction of Sb in every ML is obtained from the mass balance of incoming and leaving atoms, which depends on surface incorporation rate of new Sb atoms (considering that the surface incorporation rate of new Sb is constant during the $\text{GaAs}_{1-x}\text{Sb}_x$ layer growth and becomes zero during the $\text{GaAs}_{1-y}\text{N}_y$ growth) and on exchange rates of Sb/As (depending on exchange probabilities, temperature, etc.). It is assumed that the growth happens at a constant growth rate and that the N does not interfere in the exchange mechanism between Sb/As in the $\text{GaAs}_{1-y}\text{N}_y$ layers. The model is numerically solved layer-by-layer along the whole SL structure using a numerical iterative method. The details of the model are explained in [210].

C.2. Electronic band structure calculation

Electronic band structure simulations provide the confined energy states and then the effective bandgap of different type-II SLs structures and allow correlating period thickness and composition of the SL with their optical properties, which was performed in Section 4.2.2.3.

These simulations have been carried out at ISOM using finite differences method with the assistance of Professor Álvaro de Guzmán. Single-band effective mass approximation has been used with inputs parameters for the Sb and N contents and the period thickness of

the SLs experimentally obtained. The bandgap energy and band offset of $\text{GaAs}_{1-y}\text{N}_y$ layers were obtained considering the BAC predictions in the first-order perturbation theory [39] with the specific values for the electron effective masses described in [217]. Regarding the $\text{GaAs}_{1-x}\text{Sb}_x$ layers, their bandgap energy and band offsets were estimated using experimental results for $\text{GaAs}_{1-x}\text{Sb}_x$ pseudo-morphically grown on GaAs [67]. The hole effective mass was obtained from a linear interpolation between the binaries.

C.3. Wavefunction overlap calculation

Calculations of the electron-hole wavefunction overlaps (whose inverse value is directly proportional to the radiative lifetime) as a function of the period thickness have been carried out for type-II ($\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$) and type-I ($\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$) SLs with different period thickness (3.1 nm, 6.4 nm, 12.6 nm and 19.1 nm). All SLs have the same Sb and N contents (1.2 % N and 3.25 % Sb). These period thicknesses and contents values correspond to those of type-II SL samples introduced in Section 4.2.2, and are extracted from experimental XRD measurements shown in Figure 4.2 and Figure 4.7. The results of these simulations appear in Figure 4.12.

The calculations were carried out at IMM-CNM-CSIC by Dr. J.M. Llorens using the Nextnano++ [260].

C.4. Photocarrier extraction calculation

These simulations have been performed on type-II ($\text{GaAs}_{1-x}\text{Sb}_x/\text{GaAs}_{1-y}\text{N}_y$) SLs with 1.2 eV and 1.0 eV bandgap energies with different period thickness and also on type-I ($\text{GaAs}_{1-x-y}\text{Sb}_x\text{N}_y/\text{GaAs}$) SLs with 1.2 eV bandgap energies and different period thickness and are presented in Section 4.2.2.4.

The simulations were carried out at IEK-5 Photovoltaik Forschungszentrum in Jülich, Germany, by Dr. Urs Aeberhard. Photocarrier transport has been modeled under experimental conditions (finite built-in field and room temperature operation) using steady-state quantum-kinetic calculations based on the NEGF. The method is described in detail in references [211,261,262]. The effective masses and the band offsets for the bulk materials are obtained from the double BAC theory (see Section 2.2.3). The SLs are considered to have perfect periodicity.

For the realistic simulation of charge transport, the coupling of charge carriers to dispersionless polar optical phonons and the elastic interaction with acoustic phonons is

considered using the Fröhlich Hamiltonian and the deformation potential formalism, respectively. Photogeneration is described within linear coupling to the classical light field, while for the emission, the incoherent coupling to free field modes is considered [263]. Planar geometry is assumed, with the in-plane spatial coordinates Fourier-transformed to transverse momentum $k_{\perp}$. For the electron-phonon interaction, parameters for bulk GaAs were used, and a Kane energy of $(P_{cv})^2/(2m_0)=28.8$ eV was assumed for the light-matter coupling.

List of publications and conferences

Publications

Peer-reviewed journal publications

A. Gonzalo, A.D. Utrilla, U. Aeberhard, V. Braza, D.F. Reyes, D. Fuertes Marrón, J.M. Llorens, B. Alén, T. Ben, D. González, A. Guzman, A. Hierro and J.M. Ulloa, “*Diluted nitride type-II superlattices: overcoming the difficulties of bulk alloys in solar cells*,” Submitted to Progress in Photovoltaics.

A. Gonzalo, L. Stanojević, A.D. Utrilla, D.F. Reyes, V. Braza, D. Fuertes Marrón, T. Ben, D. González, A. Hierro, A. Guzman and J.M. Ulloa, “*Open circuit voltage recovery in GaAsSbN-based solar cells: role of deep N-related radiative states*,” Solar Energy Materials and Solar Cells 200, 109949 (2019). doi:10.1016/j.solmat.2019.109949.

N. Ruiz, V. Braza, **A. Gonzalo**, D. Fernández, T. Ben, S. Flores, J.M. Ulloa and D. González, “*Control of nitrogen inhomogeneities in type-I and type-II GaAsSbN superlattices for solar cell devices*,” Nanomaterials 9, 623 (2019). doi:10.3390/nano9040623.

N. Ruiz-Marín, D.F. Reyes, V. Braza, **A. Gonzalo**, T. Ben, S. Flores, A.D. Utrilla, J.M. Ulloa and D. González, “*Nitrogen mapping from ADF imaging analysis in quaternary dilute nitride superlattices*,” Applied Surface Science 475, 473-478 (2019). doi: 10.1016/j.apsusc.2018.12.228.

V. Braza, D.F. Reyes, **A. Gonzalo**, A.D. Utrilla, J.M. Ulloa, S. Flores, T. Ben and D. González, “*Compositional inhomogeneities in type-I and type-II superlattices for GaAsSbN-based solar cells: Effect of thermal annealing*,” Applied Surface Science 459, 1-8 (2018). doi: 10.1016/j.apsusc.2018.07.184.

U. Aeberhard, **A. Gonzalo** and J.M. Ulloa, “*Photocarrier extraction in GaAsSb/GaAsN type-II QW superlattice solar cells*,” Applied Physics Letters 112, 213904 (2018). doi: 10.1063/1.5030625.

A.D. Utrilla, D.F. Grossi, D.F. Reyes, **A. Gonzalo**, V. Braza, T. Ben, D. González, A. Guzman, A. Hierro, P.M. Koenraad and J.M. Ulloa, “*Size and shape tunability of self-assembled InAs/GaAs nanostructures through the capping rate*,” Applied Surface Science 444, 260-266 (2018). doi: 10.1016/j.apsusc.2018.03.098.

D.F. Reyes, V. Braza, **A. Gonzalo**, A.D. Utrilla, J.M. Ulloa, T. Ben and D. González, “*Modelling of the Sb and N distribution in type II GaAsSb/GaAsN superlattices for solar cell applications*,” Applied Surface Science 442, 664-672 (2018). doi: 10.1016/j.apsusc.2018.02.113.

D. González, V. Braza, A.D. Utrilla, **A. Gonzalo**, D.F. Reyes, T. Ben, A. Guzman, A. Hierro and J.M. Ulloa, “*Quantitative analysis of the interplay between InAs quantum dots and wetting layer during the GaAs capping process*,” Nanotechnology 28, 425702 (2017). doi: 10.1088/1361-6528/aa83e2.

A. Gonzalo, A.D. Utrilla, D.F. Reyes, V. Braza, J.M. Llorens, D. Fuertes Marrón, B. Alén, T. Ben, D. González, A. Guzman, A. Hierro and J.M. Ulloa, “*Strain-balanced type-II superlattices for efficient multi-junction solar cells*,” Scientific Reports 7, 4012 (2017). doi:10.1038/s41598-017-04321-4.

V. Braza, D.F. Reyes, **A. Gonzalo**, A.D. Utrilla, T. Ben, J.M. Ulloa and D. González, “*Sb and N incorporation interplay in GaAsSbN/GaAs epilayers near lattice matching condition for 1.0.-1.16 eV photonic applications*,” Nanoscale Research Letters 12, 356 (2017). doi: 10.1186/s11671-017-2129-2.

Proceeding publications

L. Stanojević, **A. Gonzalo**, A.D. Utrilla, D.F. Reyes, V. Braza, D. González, D. Fuertes Marrón, A. Hierro and J.M. Ulloa, “*Effect of capping rate on InAs/GaAs quantum dot solar cells*,” Proceedings of SPIE, Physics, Simulation, and Photonic Engineering of Photovoltaics Devices VIII 10913, 1091312 (2019). doi: 10.1117/12.2509484.

A. Gonzalo, A.D. Utrilla, U. Aeberhard, J.M. Llorens, B. Alén, V. Braza, D.F. Reyes, D. González, D. Fuertes Marron, A. Hierro and J.M. Ulloa, “*GaAsN/GaAsSb superlattices as 1 eV layers for efficient multi-junction solar cells*,” 2018 IEEE 7th World Conference on Photovoltaic Energy Conversion (WCPEC), 3463-3467 (2018). doi: 10.1109/PVSC.2018.8548015.

D.F. Reyes, V. Braza, S. Flores, N. Ruiz, A.D. Utrilla, **A. Gonzalo**, T. Ben, J.M. Ulloa and D. González, “*Effect of GaAs(Sb)(N) capping layers on (un)coupled InAs/GaAs multi-quantum dot layers for enhanced solar cells*,” 11th Advance Nanomaterials Conference, Aveiro, Portugal, July 2018.

A. Gonzalo, A.D. Utrilla, U. Aeberhard, J.M. Llorens, B. Alén, D. Fuertes Marrón, A. Guzman, A. Hierro and J.M. Ulloa, “*Type-II GaAsSb/GaAsN superlattice solar cells*,” Proceedings of SPIE, Physics, Simulation and Photonic Engineering of Photovoltaic Devices VII 10527, 105270D (2018). doi: 10.1117/12.2290079.

D.F. Reyes, V. Braza, **A. Gonzalo**, A.D. Utrilla, D.F. Grossi, P.M. Koenraad, A. Guzman, A. Hierro, J.M. Ulloa, T. Ben and D. González, “*Analysis of the Sb and N distribution in GaAsSb/GaAsN superlattices for solar cell applications*,” European Microscopy Congress 2016: Proceedings, 570-571 (2016). ISBN: 9783527808465. doi: 10.1002/9783527808465.EMC2016.6572.

A.D. Utrilla, D.F. Reyes, J.M. Llorens, **A. Gonzalo**, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Guzman, A. Hierro, and J.M. Ulloa, “*Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells*,” 32nd European Photovoltaic Solar Energy Conference and Exhibition. Proceedings, 32-35 (2016). ISBN: 3-936338-41-8. doi: 10.4229/EUPVSEC20162016-1AO.3.3.

Conference contributions

Invited oral presentations

J.M. Ulloa, **A. Gonzalo**, A.D. Utrilla, D.F. Reyes, V. Braza, J.M. Llorens, D. Fuertes Marrón, B. Alén, T. Ben, D. González, A. Guzman and A. Hierro, “*Strain-balanced type-II superlattices for efficient multi-junction solar cells*,” Bit’s Annual World Congress of Advanced Materials. Xi’an (China), June 14–16, 2017.

J.M. Ulloa, A.D. Utrilla, D.F. Reyes, **A. Gonzalo**, T. Ben, Ž. Gačević, D. González, A. Guzman and A. Hierro, “*Modified InAs/GaAs quantum dots for enhanced solar cell efficiency*,” Energy Materials and Nanotechnology Collaborative Conference on Crystal Growth. Hong Kong (China), December 14–17, 2015.

Oral presentations

S. Flores, V. Braza, D.F. Reyes, L. Stanojevic, A. Gonzalo, N. Ruiz, T. Ben, J.M. Ulloa and D. González, “*Comparative analyses of the In exchange in the InAs /GaAs QD system during the capping process with GaAs(Sb) at different growth rates,*” Microscopy at the Frontiers of Science. Granada (Spain), September 11–13, 2019.

V. Braza, D.F. Reyes, **A. Gonzalo**, N. Ruiz, S. Flores, A.D. Utrilla, T. Ben, J.M. Ulloa and D. González, “*Sb and N incorporation interplay in GaAsSbN/GaAs epilayers,*” Microscopy at the Frontiers of Science. Granada (Spain), September 11–13, 2019.

N. Ruiz, D.F. Reyes, V. Braza, S. Flores, **A. Gonzalo**, J.M. Ulloa, T. Ben and D. González, “*Formation of agglomerations in high-density multilayer InAs/GaAs quantum dots structures: the role of Sb in the capping layer,*” Microscopy at the Frontiers of Science. Granada (Spain), September 11–13, 2019.

L. Stanojević, A.D. Utrilla, **A. Gonzalo**, D.F. Reyes, D. González, D. Fuertes Marrón, A. Hierro and J.M. Ulloa, “*Improving the efficiency of InAs/GaAs quantum dot solar cells by engineering the wetting layer,*” SPIE Photonics West 2019. San Francisco, California (USA), February 1–6, 2018.

A. Gonzalo, A.D. Utrilla, U. Aeberhard, J.M. Llorens, B. Alén, V. Braza, D.F. Reyes, D. González, D. Fuertes Marrón, A. Hierro and J.M. Ulloa, “*Strain-balanced type-II superlattices for efficient multi-junction solar cells,*” 7th World Conference on Photovoltaic Energy Conversion. Waikoloa, Hawaii (USA), June 10–15, 2018.

D.F. Reyes, V. Braza, S. Flores, N. Ruiz, A.D. Utrilla, **A. Gonzalo**, T. Ben, J.M. Ulloa and D. González, “*Effect of GaAs(Sb)(N) capping layers on (un)coupled InAs/GaAs multi quantum dot layers for enhanced solar cells,*” Advanced Nanomaterials Conference 2018. Aveiro (Portugal), July 18–20, 2018.

N. Ruiz, D.F. Reyes, V. Braza, S. Flores, **A. Gonzalo**, A.D. Utrilla, J.M. Ulloa, T. Ben and D. González, “*Nitrogen mapping from ADF analysis in GaAsSb(N) superlattices for high efficient solar cells,*” XV Congreso Nacional de Materiales. Salamanca (Spain), July 4–6, 2018.

A. Gonzalo, A.D. Utrilla, U. Aeberhard, J.M. Llorens, B. Alén, D. Fuertes Marrón, A. Guzman, A. Hierro and J.M. Ulloa, “*Type-II GaAsSb/GaAsN superlattice solar cells,*” SPIE Photonics West 2018. San Francisco, California (USA), January 27–February 1, 2018.

D.F. Reyes, V. Braza, T. Ben, D. González, A.D. Utrilla, **A. Gonzalo** and J.M. Ulloa, “*Effect of thin GaAs(SbN) capping layers on (un)coupled InAs/GaAs multi-quantum dot layers for enhanced solar cells,*” 17th Conference on Defects–Recognition, Imaging and Physics in Semiconductors. Valladolid (Spain), October 8–12, 2017.

V. Braza, **A. Gonzalo**, D.F. Reyes, A.D. Utrilla, J.M. Ulloa, T. Ben, J.M. Llorens, B. Alén and D. González, “*New growth approaches to improve the performance in GaAsN-based solar cells,*” 9th International Conference on Advance Nano Materials. Aveiro (Portugal), July 19–21, 2017.

D.F. Reyes, V. Braza, A.D. Utrilla, **A. Gonzalo**, J.M. Ulloa, T. Ben and D. González, “*Effect of the capping layer composition and growth rate in the InAs quantum dots/wetting layer system,*” Microscience Microscopy Congress 2017. Manchester (United Kingdom), July 3–6, 2017.

A. Gonzalo, A.D. Utrilla, A. Arruebo, D.F. Reyes, V. Braza, J.M. Llorens, D.F. Marrón, B. Alén, T. Ben, D. González, A. Guzmán, A. Hierro and J.M. Ulloa, “*Strain-balanced type-II GaAsSb/GaAsN superlattices for efficient multi-junction solar cells,*” 41st Workshop on Compound Semiconductor Devices and Integrated Circuits held in Europe. Las Palmas de Gran Canaria (Spain), May 21–24, 2017.

A.D. Utrilla, **A. Gonzalo**, D.F. Grossi, D.F. Reyes, V. Braza-Blanco, B. Alén, D.F. Marrón, P.M. Koenraad, T. Ben, D. González, A. Guzmán, A. Hierro and J.M. Ulloa, “*Strain-balanced type-II GaAsSb/GaAsN superlattices as 1 eV layer for efficient multi-junction solar cells,*” 19th International Conference on Molecular Beam Epitaxy. Montpellier (France), September 4–9, 2016.

D.F. Reyes, V. Braza, **A. Gonzalo**, A.D. Utrilla, D.F. Grossi, P.M. Koenraad, A. Guzman, A. Hierro, J.M. Ulloa, T. Ben and D. González, “*Analysis of the Sb and N distribution in GaAsSb/GaAsN superlattices for solar cell applications,*” 16th European Microscopy Congress. Lyon (France), August 28–September 2, 2016.

A.D. Utrilla, D.F. Reyes, J.M. Llorens, **A. Gonzalo**, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Guzman, A. Hierro and J.M. Ulloa, “*Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells,*” European Photovoltaic Solar Energy Conference and Exhibition 2016. München (Germany), June 20–24, 2016.

V. Braza, D.F. Reyes, **A. Gonzalo**, A.D. Utrilla, J.M. Ulloa, A. Hierro, A. Guzman, T. Ben and D. González, “*Análisis de la interdifusión en superredes de GaNAsSb para*

aplicaciones en celdas solares de multiunión,” XIV Congreso Nacional de Materiales. Gijón (Spain), June 8–10, 2016.

Poster presentations

N. Ruiz, D.F. Reyes, V. Braza, T. Ben, S. Flores, **A. Gonzalo**, L. Stanojević, J.M. Ulloa and D. González, “*Influence of GaAsSb capping layers on the vertical-alignment in closely stacked InAs/GaAs multi quantum dots,*” Microscience Microscopy Congress. Manchester, (UK), July 1–4, 2019.

D. Tjeertes, **A. Gonzalo**, J.M. Ulloa, M.S. Sharma, M. Felici, F. Biccari, M. Gurioli and P.M. Koenraad, “*Hydrogen Passivation of N:GaAs Studied by Cross-Sectional Scanning Tunneling Microscopy,*” 21st International Conference on Microscopy of Semiconducting Materials. Cambridge, (UK), April 9–12, 2019.

N. Ruiz Marín, D.F. Reyes, V. Braza, S. Flores, **A. Gonzalo**, J. María Ulloa, A.D. Utrilla, T. Ben and D. González, “*Analysis of the N distribution in GaAs(Sb)(N) superlattices from ADF imaging,*” 21st International Conference on Microscopy of Semiconducting Materials. Cambridge, (United Kingdom), April 9–12, 2019.

V. Braza, D.F. Reyes, A.D. Utrilla, **A. Gonzalo**, T. Ben, J.M. Ulloa and D. González, “*Evolution of InAs quantum dots/wetting layer system under different GaAs capping layer growth rates,*” 20th Microscopy of Semi Conducting Materials. Oxford (United Kingdom), April 9–13, 2017.

A. Gonzalo, A.D. Utrilla, D.F. Reyes, V. Braza-Blanco, B. Alén, D.F. Marrón, T. Ben, D. González, A. Guzmán, A. Hierro and J.M. Ulloa, “*Strain-balanced type-II GaAsSb/GaAsN superlattices for efficient multi-junction solar cells,*” 32nd North American Conference on Molecular Beam Epitaxy. Saratoga Springs, New York (USA), September 18–21, 2016.

A.D. Utrilla, **A. Gonzalo**, J.M. Llorens, A. Guzman, A. Hierro and J.M. Ulloa, “*Role of the wetting layer in the performance of quantum dot solar cells,*” 2016 European Materials Research Society Spring Meeting. Lille (France), May 2–6, 2016.

A. Gonzalo, A.D. Utrilla, D.F. Reyes, V. Braza-Blanco, D. Fuertes Marrón, T. Ben, D. González, A. Guzman, A. Hierro and J.M. Ulloa, “*Strain-balanced GaAsSb-GaAsN type-II superlattices as 1eV layer for efficient multi-junction solar cells,*” 2016 European Materials Research Society Spring Meeting. Lille (France), May 2–6, 2016.

Conference awards

Winner of the 2nd Poster Prize in the Symposium “Strained Layers and Quantum Wells” at 20th Microscopy of Semi Conducting Materials Conference: V. Braza, D.F. Reyes, A.D. Utrilla, **A. Gonzalo**, T. Ben, J.M. Ulloa and D. González, “*Evolution of InAs quantum dots/wetting layer system under different GaAs capping layer growth rates,*” 20th Microscopy of Semi Conducting Materials. Oxford (United Kingdom), April 9–13, 2017.

Winner of the Student Award for “the most outstanding student research work in the field of New Materials and Concepts for Cells” at 2016 European Photovoltaic Solar Energy Conference and Exhibition: A.D. Utrilla, D.F. Reyes, J.M. Llorens, **A. Gonzalo**, I. Artacho, T. Ben, D. González, Ž. Gačević, A. Guzman, A. Hierro and J.M. Ulloa, “*Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells,*” European Photovoltaic Solar Energy Conference and Exhibition 2016. Munich (Germany), June 20-24, 2016.

Winner of Best poster Award in the Symposium “Advanced materials and Characterization Techniques for Solar Cells III” at the 2016 European Materials Research Society Spring Meeting: **A. Gonzalo**, A.D. Utrilla, D.F. Reyes, V. Braza-Blanco, D. Fuertes Marrón, T. Ben, D. González, A. Guzman, A. Hierro and J.M. Ulloa, “*Strain-balanced GaAsSb-GaAsN type-II superlattices as 1eV layer for efficient multi-junction solar cells,*” 2016 European Materials Research Society Spring Meeting. Lille (France), May 2–6, 2016.

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