UNIVERSIDAD POLITÉCNICA DE MADRID

**ESCUELA TÉCNICA SUPERIOR
DE INGENIEROS DE TELECOMUNICACIÓN**

TESIS DOCTORAL

**CONTRIBUTIONS TO THE DEVELOPMENT OF
NOVEL SOLAR CELLS CONCEPTS
CONTRIBUCIONES AL DESARROLLO DE
NUEVOS CONCEPTOS DE CÉLULAS SOLARES**

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Licenciado en Ciencias Físicas
2017

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**Instituto de Energía Solar
Departamento de Electrónica Física
Escuela Técnica Superior de Ingenieros de Telecomunicación**

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A Noelia, por serlo todo.

$$B > \frac{1}{n} \sum_{i=1}^n x_i ,$$

(be greater than average)

*“Briefly summarized, what I did can be described
as simply an act of desperation.”*

— Max Planck

Quisiera dedicar unas palabras de agradecimiento a aquellos que han hecho esta tesis doctoral posible. Tengo el orgullo de haber realizado mi tesis en el Instituto de Energía Solar, un centro de investigación excelente que acoge a un personal sobresaliente. Para poder llevarlo a cabo he disfrutado de un contrato de Formación de Personal Investigador, que por contra a lo que gran parte de la sociedad piensa de este tipo de contratos, he recibido gracias a mis méritos y esfuerzo desde que inicié mis estudios, y no por ningún trato de favor personal. Es algo de lo que estoy orgulloso.

Una tesis doctoral no solo se trata de realizar un proyecto de investigación, se trata de formar a investigadores, a personas que puedan aportar su experiencia a la sociedad que les rodea. En este sentido, Antonio Martí e Íñigo han sido los responsables (culpables) de moldearme en estos años. En primer lugar debo agradecer a Antonio, quien tiene mi respeto y mi afecto, y siempre lo tendrá, pero no porque sea el jefe del grupo ni mi tutor o director de tesis, sino porque el respeto hay que ganárselo, y él se lo gana diariamente, como científico, “*siempre tiene razón*”, y como persona, siempre atento y gentil con los suyos, y yo me he sentido como uno de los suyos. Íñigo tiene una capacidad de enseñanza infinita, siempre dispuesto a dedicarte unos (bastantes) minutos a explicarte cada detalle de un experimento o de un concepto. Inducido por Antonio, siempre persigue la perfección en aquello que se propone, pero no para buscar el éxito, sino por el simple hecho de la recompensa del trabajo bien hecho. Espero poder seguir aprendiendo de ellos.

El grupo de investigación en el que he desarrollado esta tesis lo forman un grupo de personas extraordinarias. A Alejandro le debo el primer contacto experimental de mi paso por el IES, él te enseña, te da la confianza y responsabilidad para que desarrolles tu trabajo libremente. Siempre dispuesto a aconsejarte. Pablo y Elisa son un tándem de sabiduría, trabajo y conocimiento que han intentado transmitir en cada ocasión que he compartido con ellos. La ayuda de Irene es inestimable, ayudando en lo que haga falta y dispuesta a resolverte cualquier problema. Gracias a Esther por todas las explicaciones y conversaciones que me han aclarado multitud de detalles a lo largo de estos años, sin perder la sonrisa en la cara. Gracias también al resto de integrantes del grupo.

Del resto de grupos del IES me gustaría agradecer en particular a Iván García y Luis Cifuentes las múltiples conversaciones sobre aspectos puntuales del procesado de células solares, también a Jesús, siempre dispuesto a echarte una mano. Gracias a Mario por toda la ayuda en la escritura de esta Tesis con $\text{\LaTeX}$. Gracias también a Marta Victoria por su colaboración con medidas ópticas. A Rubén, que me dio las primeras nociones con SMARTS. Gracias a Gabriel Sala e Ignacio Antón por todas las aclaraciones y consejos con los análisis de eficiencias. Agradezco la disposición de Estefanía para resolver cualquier duda con el dichoso programa de doctorado.

Gracias al resto de compañeros del IES. Personalmente, me quedo con la amistad de Fran, que espero que podamos seguir teniendo mucho tiempo. También agradezco a la gente del Comunio por los buenos ratos que pasamos. Gracias al personal administrativo y de mantenimiento del IES por el engorroso trabajo que hacen por nosotros.

Quisiera acordarme de mis orígenes y agradecer a Luis Labajos, magnífico profesor, que me introdujo en la investigación, y a a Julio Cárabe y Rocío Barrio por permitirme iniciarme en el mundo de la fotovoltaica sin esperar nada a cambio.

He de agradecer a mi madre, que confía en mi buen hacer en la vida y que se preocupa, a su manera. A mi hermana Neni y Edu, que me acogieron en su casa cuando lo necesité. A Cande, por preocuparse de sus hermanos. Y a Pupe, que además de su alegría, me ha ayudado a la corrección lingüística de esta Tesis.

A mis amigos de Badajoz, que esta época en Madrid tanto tiempo nos ha separado y que me recargan las pilas cada vez que nos vemos. En especial estoy orgulloso de la amistad de Carlos, que siempre estará ahí cuando le necesite, bondadoso, generoso, equilibrado, buena persona. También agradezco a mi familia política cacereña por todo el apoyo que me han dado, tratándome desde el primer día como si fuera un hijo más.

Por último, estos agradecimientos no son nada comparado a todo lo que le debo a Noelia y que no caben en unas simples líneas. Gracias a ella he podido llegar, al menos, hasta aquí. Sin ella nada, nada habría sido posible. Ella es la persona que equilibra mi vida, sabes que sin ti estaría perdido. Espero poder devolverte todo lo que me has dado y que el tiempo de trabajo nos ha quitado. Gracias.

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Resumen

Esta Tesis contribuye al desarrollo de nuevos conceptos de células solares. Estos nuevos conceptos son aquellas propuestas tecnológicas que no están sujetas al límite de Shockley-Queisser (S-Q), pudiendo sobrepasarlo. Dentro de estas nuevas propuestas tecnológicas, la más avanzada y que hoy en día ya se aplica a nivel industrial es la célula solar de multiunión (MJSC, por sus siglas en inglés). El récord de eficiencia de conversión experimental de las MJSCs es del 46.0 % bajo 508 soles de concentración publicado en 2014. Además, otras propuestas tecnológicas fueron planteados y se englobaron en lo que se conoce como “células solares de tercera generación”, que estaban en investigación y desarrollo y que no se aplicaban a nivel industrial. De estas propuestas en fotovoltaica (PV, por sus siglas en inglés) como nuevos conceptos de células solares, la más desarrollada es la célula solar de banda intermedia (IBSC, por sus siglas en inglés). La eficiencia límite teórica de la IBSC es del 63.2 % bajo máxima concentración y asumiendo el Sol como un cuerpo negro a 6000 K. La tecnología más estudiada para implementar las IBSCs ha sido la de puntos cuánticos (QDs, por sus siglas en inglés), denominadas células solares de banda intermedia basadas en puntos cuánticos (QD-IBSC, por sus siglas en inglés). Hasta ahora, los mayores retos de las IBSCs se han enmarcado en demostrar sus principios operacionales, lo cual ya ha sido conseguido a baja temperatura y, más recientemente, a temperatura ambiente. Sin embargo, a pesar de los esfuerzos en la investigación de QD-IBSCs y sus avances, éstas siguen presentando dos problemas principales que disminuyen su rendimiento: una ineficiente absorción de fotones con energías menores que la banda prohibida (E_G) –fotones sub-banda prohibida– y una excesiva degradación del voltaje de operación de la IBSC comparada con una célula

de referencia (aquella fabricada con la misma estructura de semiconductor, pero en la que se ha remplazado la estructura de QDs que induce la banda intermedia (IB, por sus siglas en inglés) por un material semiconductor convencional).

En este contexto, nuestro trabajo se centra en contribuir al desarrollo y mejora de QD-IBSCs viables. Hemos propuesto e investigado la incorporación de técnicas de atrapamiento de luz basadas en texturar el sustrato de QD-IBSCs de alta banda prohibida, fabricadas con QDs de InAs en una matriz de AlGaAs, es decir, InAs/AlGaAs QD-IBSCs. A través de una amplia caracterización de las InAs/AlGaAs QD-IBSCs texturadas, demostramos que los dispositivos de QD-IBSCs texturados muestran una mejora en la absorción de fotones con energías por debajo de la banda prohibida. Asimismo, los dispositivos basados QD-IB pueden ser utilizados como detectores de radiación infrarroja, a partir del concepto de fotodetector de infrarrojos activado ópticamente (OTIP, por sus siglas en inglés). Nuestro texturado aplicado a dispositivos de InAs/AlGaAs QD-IB también mejora la fotodetección en el rango 3-5 μm .

En relación al concepto de IBSC, hemos ampliado la caracterización QD-IBSCs, mostrando por primera vez el fenómeno de fotovoltaje con dos fotones sub-banda prohibida en prototipos de GaSb/GaAs QD-IBSC. Este fenómeno es análogo al de fotocorriente con dos fotones sub-banda prohibida, en el que en lugar de medir el incremento de la fotocorriente debida a añadir una segunda fuente de iluminación sub-banda prohibida, se mide el incremento del fotovoltaje. Gracias a ello hemos podido mejorar la comprensión del marco teórico de las IBSCs.

Además, esta Tesis contribuye al desarrollo de un nuevo método de procesamiento de células solares delgadas basadas en semiconductores III-V compatibles con caracterización a baja temperatura y que es aplicable a QD-IBSC basadas en InAs/AlGaAs. Siguiendo este método, hemos fabricado y caracterizado células solares delgadas de AlGaAs. Mostramos la adecuación de este método para medir a bajas temperaturas mediante la medida de fotocorriente o eficiencia cuántica de los dispositivos a diferentes temperaturas.

Finalmente, la última parte de esta Tesis contribuye al entendimiento del otro concepto de células solares que ya hemos introducido al comienzo, las MJSCs. Hemos

estudiado la eficiencia límite de la producción de energía anual (AEE, por sus siglas en inglés) de las MJSC, haciendo una comparación entre las MJSC conectadas en serie (MJSC-SC, por sus siglas en inglés) –presentando dos terminales eléctricos para su conexión– y las MJSC independientemente conectadas (MJSC-IC, por sus siglas en inglés) –presentando dos terminales para cada sub-célula que forme parte de la multiunión–. La eficiencia límite de conversión fotovoltaica para estos sistemas tandem se ha revisado siguiendo un análisis de balance detallado. Los resultados obtenidos nos confirman, por un lado, lo ya sabido: que las MJSC-IC tienen una mayor eficiencia que las MJSC-SC. Además, discutimos acerca del concepto de la AEE con el fin de analizar la optimización de dichas MJSC. Debido a la eliminación de la restricción de la conexión en serie (que hace que la corriente a través de cada sub-célula en la unión sea la misma) en MJSC-IC, éstas también muestran una mayor AEE que las MJSC-SC para el mismo número de células solares. A partir de estos resultados, podemos concluir que sería más conveniente pasar de un sistema de 4-MJSC-SC a uno de 4-MJSC-IC en lugar de aumentar el número de sub-celulas. Esta tendencia se mantiene para un mayor número de células que forman la multiunión.

Finalmente, con objeto de contribuir a la capacidad de fabricación y caracterización del Instituto de Energía Solar de la Universidad Politécnica de Madrid (IES-UPM), hemos desarrollado un sistema de electrodeposición para aplicar revestimiento de metales a las células solares y un sistema de caracterización de reflectancia-transmitancia mediante una esfera integradora.

Abstract

This Thesis contributes to the development of novel solar cells concepts. These novel concepts are not subjected to the Shockley-Queisser (S-Q) limit since they are capable of exceeding it. In this respect, the most advanced technology and that nowadays it is already applied at industry level is that of multi-junction solar cell (MJSC). MJSC shows an experimental conversion efficiency of 46.0 % under 508 suns of concentration reported in 2014. In addition, other technological approaches were proposed and were encompassed in what was known as “third generation solar cells”. These technological proposals were under research and development, and they were not applied at industry level. From these approaches in photovoltaic (PV) as a novel solar cell concepts, the most developed is the intermediate band solar cell (IBSC). The limiting efficiency of the IBSC is 63.2 % under maximum solar concentration (blackbody at 6000 K). The most studied technology for implementing IBSC have been those based on quantum dots (QD)s, which are named quantum dot-intermediate band solar cells (QD-IBSC)s. Up until now, the greatest challenges in IBSC have been to prove the two operation principles of the IBSC what has been achieved, firstly, at low temperature, and, recently, at room temperature. Despite the efforts in QD-IBSCs researchs and their advances, the main problems still curb the performance of IB solar cells: the inefficient absorption of photons with energy lower than the bandgap (E_G) –sub-bandgap photons– and the excessive operation voltage degradation of the IBSC compared with the reference solar cell (that fabricated with the same semiconductor structure, but in which the QD structure that induces the intermediate band (IB) has been replaced by a conventional semiconductor material).

In this context, our work focuses on the contribution to the development and the enhancement of practical QD-IBSCs. We have proposed and investigated the inclusion of light-trapping techniques based on texturing the substrate of wide-bandgap QD-IBSCs, fabricated with InAs QDs in AlGaAs host semiconductor, that is, InAs/AlGaAs QD-IBSC. By doing an extensive characterization of the textured InAs/AlGaAs QD-IBSC, we demonstrate an improvement in the absorption of sub-bandgap photons. In addition, QD-IB devices can be employed as infrared (IR) photodetectors, from the concept of optically triggered infrared photodetector (OTIP). The texturing applied to InAs/AlGaAs QD-IB devices also enhances the photodetection in the range 3-5 μm .

Regarding the topic of IBSCs, we have extended the characterization of QD-IBSCs, showing for the first time the two-photon photovoltage (TPPV) phenomenon, that is, the production of photovoltage by means of two sub-bandgap photon illumination in GaSb/GaAs QD-IBSC. This phenomenon is similar to the two-photon photocurrent phenomenon in which instead of measuring the increment of photocurrent due to the addition of a second sub-bandgap photon source, an increment in photovoltage is measured. This two-photon photovoltage phenomenon represents a key demonstration in IBSCs which had been elusive until now. It allows to better comprehension of the IBSC framework.

In addition, this Thesis contributes to the development of a new processing method of thin-film solar cells based on III-V semiconductors compatible with low-temperature characterization and also applicable with the processing of InAs/AlGaAs QD-IBSCs, by virtue of its importance in the characterization of electronic devices based on nanostructures, such as QD-IB devices. Following this method, we have fabricated and characterized thin-film AlGaAs solar cells. We show the adequacy of this method to measure at low temperatures the photocurrent or quantum efficiency of the devices.

Finally, the last part of this Thesis contributes to the understanding of the other high-efficiency solar cell concepts, already presented, the MJSCs. We have studied the limiting efficiency of the annual energy production (AEE) of MJSCs, making a comparison between MJSC series-connected (MJSC-SC) –having two electric external terminals for their connection– and independently-connected ones (MJSC-IC) –having

two electric external terminals for the connection of each sub-cell-. The efficiency of photovoltaic conversion for tandem systems are revised through a detailed balance analysis. MJSC-IC have a greater photovoltaic conversion efficiency than MJSC-SC, what is well-known. In addition, we also discuss the concept of AEE in order to analyze the optimization of the MJSC. Due to the removal of the series connection constrain, MJSC-ICs also show higher AEE than MJSC-SCs for the same number of cells. From the results, we can conclude that implementing several terminals to a four junctions MJSC-SC, converting it into a MJSC-IC offers a higher AEE gain than implementing a five junctions MJSC-SC. This trend is maintained for a greater number of sub-cell of the tandem.

In order to contribute to the fabrication and characterization capabilities of the Instituto de Energía Solar of the Universidad Politécnica de Madrid (IES-UPM), we have developed an electroplating set-up for the deposition of metal on solar cells and a reflectance-transmittance characterization set-up by using an integrating sphere.

Nomenclature

λ	Photon wavelength [nm]
μ	Radiation chemical potential [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$] / [eV]
μ_{CI}	Chemical potential of the photons emitted via CB $\rightarrow$ IB recombination; $\varepsilon_{\text{Fe}} - \varepsilon_{\text{FIB}}$ [eV]
μ_{CV}	Chemical potential of the photons emitted via CB $\rightarrow$ VB recombination; $\varepsilon_{\text{Fe}} - \varepsilon_{\text{Fh}}$ [eV]
μ_{IV}	Chemical potential of the photons emitted via IB $\rightarrow$ VB recombination; $\varepsilon_{\text{FIB}} - \varepsilon_{\text{Fh}}$ [eV]
ν	Photon frequency [Hz]
ε	Energy [eV]
ε_{FC}	Quasi-Fermi level for electrons in the CB [eV]
ε_{FIB}	Quasi-Fermi level for electrons in the IB [eV]
ε_{FV}	Quasi-Fermi level for holes in the VB [eV]
ε_{F}	Fermi level [eV]
ε_{i}	Fermi level for an intrinsic semiconductor [eV]
c	Speed of light in vacuum; 2.99792458×10^8 [m s^{-1}]

e	Elementary charge; $1.60217657 \times 10^{-19}$ [C]
E_{ES}	Energy of the transition from the first ES for holes to $\text{ES}1_e$ in a QD [eV]
E_{G}	Bandgap of a semiconductor [eV]
E_{H}	Larger of the two sub-bandgaps in an IB material [eV]
E_{L}	Smaller of the two sub-bandgaps in an IB material [eV]
E_{QD}	Bulk-material bandgap of a QD material [eV]
E_{WL}	Bandgap of the WL in a QD material grown in the S-K mode [eV]
h	Planck's constant; $6.58211928 \times 10^{-16}$ [eV s]
I	Solar-cell current [mA]
J	Solar-cell current density [mA cm^{-2}]
J_{L}	Photo-generated current density [mA cm^{-2}]
J_{SC}	Short-circuit current density [mA cm^{-2}]
k	Boltzmann constant; 8.6173324×10^{-5} [eV K $^{-1}$]
q	Electric charge of an electron; $-e$ [C]
RT	Room temperature [K]
T	Temperature [K]
V	Voltage / Output voltage of a solar cell [V] / [V]
V_{bias}	Voltage bias [V]
V_{OC}	Open-circuit voltage [V]

List of Acronyms

AEE annual energy production efficiency

AM air mass

CB conduction band

CPV concentrating photovoltaics

EDX Energy Dispersive X-ray

EQE External Quantum Efficiency

FDL field-damping layer

HRTEM High-resolution TEM

IB intermediate band

IBSC intermediate band solar cell

IES Instituto de Energía Solar

IMM Instituto de Microelectrónica de Madrid (CSIC)

INA Institute of Nanoscience of Aragon

IR infrared

MBE molecular beam epitaxy

MJSC multi-junction solar cell

MJSC-IC Multi-junction solar cell independently connected

MJSC-SC Multi-junction solar cell series connected

MOCVD metalorganic chemical vapour deposition

MOVPE metalorganic vapour phase epitaxy

NRR non-radiative recombination

OTIP optically triggered infrared photodetector

PC photocurrent

PV photovoltaic

QD quantum dot

QD-IB quantum-dot intermediate band

QD-IBSC quantum-dot IBSC

QFL quasi-Fermi level

S-I semi-insulating

S-K Stranski-Krastanov

SAED Selected Area Electron Diffraction

SEL stop etching layer

SEM Scanning Electron Microscope

SGSC single-gap solar cell

SQ Shockley and Queisser

STEM Scanning-TEM

STEM-HAADF STEM-High Angle Annular Dark Field

TEM transmission electron microscopy

TPPC *two-photon photocurrent*

TPPV *two-photon photovoltage*

UPM Universidad Politécnica de Madrid

VB valence band

VBO valence band offset

WL wetting layer

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Chapter 1

Introduction and background

In 2015, the global energy consumption increased 1 % from the consumption in 2014, which was 13699 Mtoe¹. Only 1.35 % of this increase was produced by some renewable energy source, which includes photovoltaic (PV) solar energy [OEC]. Despite this rate from the overall energy analysis, PV is one of the most promising [BP,NRE] source of renewable energy and one of the fastest-growing renewable electricity technologies. In this respect in 2015, global solar PV power generating capacity increased by more than 50 GW, which represents an increment of 28 % versus the end of 2014 and leads the global solar PV capacity to 231 GW [BP,NRE]. There are some elements which impact the final cost of PV solar energy, such as the fabrication of the solar cell, the module, the inverter, etc. In particular, improving the conversion efficiency of solar cells is one of the different strategies that are being followed in order to make the PV solar energy more competitive than classical energy sources.

A conventional semiconductor single-gap solar cell (SGSC) has a conversion limiting efficiency, known as the Shockley and Queisser (SQ) limit, of 40.7 % under 6000 K blackbody radiation and maximum solar concentration; and 30.5 % under blackbody radiation and one sun [Sho 61, Ara 94]. These efficiencies are obtained assuming that: (1) all photons with energies higher than E_G , the energy bandgap of the semiconductor, are absorbed, (2) carrier mobility is infinity and therefore ohmic losses are neglected, and

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¹1 Mtoe is equivalent to 8.598×10^{-5} GWh.

(3) all recombination is radiative. Efficiencies close to the SQ limit have been already reported: 28.8 % in gallium arsenide one sun solar cells obtained by Alta Devices measured under AM1.5 global spectrum [Gre 15]. To surpass the SQ limit, enhance solar cell performance, and achieve low-cost PV, different novel solar cell concepts have been developed in the last years. These new solar cells concepts are not subjected to the SQ limit. They are capable of exceeding it by reducing thermal² and transmission³ losses, which are the main limiting factors in conventional SGSCs. In this respect, the most advanced technology and that nowadays it is already applied at industry level is that of multi-junction solar cell (MJSC) [Jac 55]. MJSCs have reached a very mature stage, where an experimental conversion efficiency of 46.0 % under 508 suns of concentration has been reported in 2014 by SOITEC, CEA-Leti, and ISE-Fraunhofer [ISE].

Besides MJSCs, other approaches in PV having the potential of exceeding the SQ limit have been studied, although they are in a less mature state. They were encompassed in what is known as “third generation solar cells” [Luq]. These include the hot-carrier solar cell [Ros 82, Wur 97], the multiple exciton generation solar cell [Noz 02], and the intermediate band solar cell (IBSC) [Luq 97]. Among these three, the IBSC concept, characterized by a 63.2 % limiting efficiency under maximum solar concentration (blackbody at 6000 K), is the one most developed. In this introductory chapter, our intention is to present and summarize briefly the IBSC concept and its characteristics since the IBSC will be the main scope of some of the investigations carried out in this Thesis. Complete and extended explanations about the IBSC can be founded elsewhere in the literature [Luq 06, Sog 06, Luq 12, Oka 15].

1.1 Introduction to the IBSC

The IBSC concept was proposed by A. Luque and A. Martí in 1997 [Luq 97]. It exploits the optoelectronic properties of intermediate band (IB) materials. An IB material

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²Thermal losses are produced on account of carriers photogenerated by photons with energy higher than the energy bandgap, E_G , that relax to the bottom of the conduction band and the top of the valence band, losing their excess of energy as heat before they are extracted as photocurrent.

³Transmission losses are due to the non absorption of photons with energy lower than the E_G .

is a semiconductor material which includes an IB located in between the conduction band (CB) and the valence band (VB). In this IB material, besides the bandgap between CB and VB of the semiconductor, E_G , the IB induces two additional sub-bandgaps, E_H (the larger one) and E_L (the lower one), as depicted in Figure 1.1, independently of which sub-bandgap is the upper or lower one. Consequently, in addition to the common supra-bandgap absorption of photons, with energy $h\nu > E_G^4$, by electron transitions between the CB to the VB (indicated as transition 3), sub-bandgap absorptions of photons might occur among the three bands. The sub-bandgap absorptions can take place when an electron interacts with photons with energy higher than the sub-bandgaps. The transitions between the CB and the IB (transition 1) and between the IB and the VB (transition 2) are indicated in Figure 1.1.

Figure 1.1: Simplified band diagram of an IB material. Several magnitudes are represented: the three bands (VB, IB and CB), the three bandgaps (E_G , E_H and E_L)—with dashed arrows—, the three QFLs (ε_{FV} , ε_{FC} and ε_{FI}) —with dashed lines—, and three possible interband transitions —with arrows— are indicated. Electrons are depicted with filled circles and holes with empty circles.

A basic sketch of the IBSC and its band diagram are depicted in Figure 1.2. An IBSC consists of a sandwiched IB material between two semiconductors, one p-type and one n-type, acting as selective contacts [Wur 82]. The selective contacts allow ideally the collection of only holes from the VB through the p-layer and only electrons from the CB through the n-layer. The electronic population of the three bands can be described

⁴ h is the Planck's constant and ν is the frequency of the photon.

by three separate quasi-Fermi levels (QFLs), ε_{FV} for the VB, ε_{FC} for the CB and ε_{FI} for the IB. The energy delivered to the external circuit per electron, which is the output voltage, V , times e , equals to μ_{CV} , where e is the electron charge, and μ_{CV} is equal to the QFL split between ε_{FC} in the n-side and ε_{FV} in the p-side. Two additional QFL splits are defined as $\mu_{IV} = \varepsilon_{FI} - \varepsilon_{FV}$, and $\mu_{CI} = \varepsilon_{FC} - \varepsilon_{FI}$. As in conventional SGSC, the output voltage V is still limited by E_G and, assuming that the three QFLs are constant through the solar cell, they are related to V as follows:

$$\mu_{CV} = \mu_{CI} + \mu_{IV} = eV \quad (1.1)$$

As we have advanced, the IBSC produces photocurrent (PC) from the absorption of photons with energy higher than E_G and the absorption of sub-bandgap photons through the IB in a two-step process. In order to assure the absorption of sub-bandgap photons, the IB must be partially filled with electrons (that is, ε_{FIB} must be located inside the IB), so that it has empty states to receive electrons from the VB as well as electrons to be promoted to the CB exist. To achieve the ideal IBSC it is also required that only one of the three interband transitions is possible for a given photon energy. In other words, the absorption coefficients for each transition, α_{IV} , α_{CI} , and α_{CV} ⁵, do not overlap among them, if the bandgap distribution is optimized [Lpe 16]. This is called ideal photon selectivity. In addition, complete photon absorption is assumed.

From what we have just described, we can summarize the two key operation principles of an IBSC as follows:

- Two-photon sub-bandgap photocurrent: an IBSC can produce photocurrent from the absorption of sub-bandgap photons in a two-step process that involve the IB.
- Voltage preservation: the output voltage of an IBSC under operation is not limited by either of the two sub-bandgaps, E_H or E_L .

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⁵ α_{IV} is the absorption coefficient for transitions between the VB and IB; α_{CI} is the absorption coefficient for transitions between the IB and CB; and α_{CV} is the absorption coefficient for transitions between the VB and CB

Figure 1.2: (Top) Basic sketch of an IBSC and (bottom) its simplified band diagram under operation. The output voltage, V , determined by μ_{CV}/e , and the photocurrent, J , are indicated.

Comparing an IBSC to a SGSC, we realize that an IBSC can maintain the broad absorption of a low bandgap solar cell while it preserves the voltage of a high bandgap solar cell. This fact is illustrated in Figure 1.3, where the current density-voltage ($J-V$) characteristics of an ideal IBSC and SGSC are depicted. The two operation principles of the IBSC can be understood as follow: an ideal IBSC can deliver a higher PC (red curve) than a SGSC (blue curve) without degrading its open-circuit voltage, consequently with a greater efficiency limit. It is possible to achieve higher PCs (black and green curves) in SGSCs at the cost of reducing their open-circuit voltages and consequently their conversion efficiencies. This idea is one of the main points of the IBSC concept, where the trade-off between current and voltage is relaxed and the maximum conversion efficiency of the IBSC surpasses the SQ limit.

In Figure 1.4 the limiting efficiency achievable with the IBSC, working in the radiative limit, is represented. This limiting efficiency has been obtained from detailed balance arguments and solving the $J = J(V)$ equations for the IBSC [Sho 61, Luq 97].

Figure 1.3: Comparison of the current density-voltage characteristics under maximum concentration ($X = 46050$) of an ideal IBSC (red curve) and an optimum SGSC ($E_G = 1.11$ eV, black curve). Two additional curves for the $J - V$ characteristic of single gap solar cell are represented for comparison: one with the same total bandgap as the IBSC ($E_G = 1.95$ eV, blue curve) and one with a smaller bandgap ($E_G = 0.71$ eV, green curve).

In addition to the the IBSC limiting efficiency, the limiting efficiency for SGSC and a two series-connected tandem solar cell are shown. The results are obtained for the solar cells illuminated with a blackbody solar spectrum at $T_s = 6000$ K and maximum sunlight concentration ($X = 46050$). The optimal bangap distribution for an IBSC are $E_G = 1.95$ eV, $E_H = 1.24$ eV, and $E_L = 0.71$ eV, which leads to a limiting efficiency of 63.2 %. This value is substantially greater than that of the SGSC (40.8 %) and of the two series-connected tandem solar cell (55.9 %).

The two key principles of operation of an IBSC are better comprehended by looking at the simplified equivalent electric circuit of the solar cell depicted in Figure 1.5. This circuit represents the ideal case of an IBSC in which series and paralel resistances, and absorption coefficient overlap are neglected. The current density generators represent

Figure 1.4: Detailed balance efficiency limit of an IBSC compared to that of a SGSC and a two series-connected tandem solar cell. The efficiency is represented as a function of the lowest bandgap in each structure. The corresponding values of the highest bangap involved in each structure is indicated. This figure is adapted from [Luq 97].

the optical transitions associated to the absorption of photons and the diodes represent the radiative recombination processes. The ideal IBSC, working in the radiative limit, can be interpreted as one solar cell with bandgap E_G , which produces a current density J_3 , connected in parallel with two series-connected solar cells with bandgaps E_H and E_L , which produce current densities of J_1 and J_2 , respectively. As they are series-connected, $J_1 = J_2$. The two-photon sub-bandgap absorption implies that the total current density, J , is greater than J_3 , while the output voltage V , equal to μ_{CV}/e , is preserved [Luq 04].

The concepts expressed and explained above are sufficient to reach a general overview of the IBSC concept and to follow the rest of this introductory chapter. As it was

Figure 1.5: Equivalent circuit of an ideal IBSC. The diodes represent the radiative recombination and the current generators represent the optical transitions associated to carrier generation.

mentioned before, extended explanations about the IBSC theory can be found elsewhere [Luq 97, Luq 06, Sog 06, Luq 12, Oka 15].

1.2 Implementation of IBSCs

An IB material has to be engineered, because no conventional semiconductor behaves as such. Different approaches to reach this technological challenge have been proposed and investigated: nanostructures, such as for example quantum dot (QD) [Mar 00], highly mismatched alloys (HMAs) [Sha 99], and deep level impurities (DLIs) in semiconductor bulk materials [Luq 06]. They are schematically represented in Figure 1.6.

Briefly, semiconductor bulk materials with high density of DLIs, exceeding the Luque limit⁶ [Luq 06], lead to the delocalization of the wavefunction of the electrons. DLIs allow an IB to be formed and inhibits non-radiative recombination, which degrades the performance of solar cells. On another note, HMAs are semiconductor alloys

⁶The Luque limit is the concentration of carriers at which the wavefunctions of the electrons delocalize.

Figure 1.6: The three technological approaches for implementing IB materials: (a) QDs, (b) DLIs, and (c) HMAs. The drawings at the top illustrate the physical implementation of the IB materials and the bottom ones depict a simplification of the band diagram for each one, where ε is the axis representing the direction in which energy increases. The direction of growth is also indicated with an arrow. The QDs layers are indicated in black, the impurities for the DLIs are depicted in green, and the foreign elements for HMAs are represented in blue.

containing isoelectronic elements with highly electronegative impurity atoms, which induce changes in the CB, splitting its energy band into E_+ and E_- . This phenomenon is explained by the band-anticrossing model, and from the perspective of an IB material, E_- would act as the IB and E_+ as the CB [Sha 99, Wal 00]. These two technological approaches will be outside of the scope of this Thesis.

QDs were proposed by Martí et al. [Mar 00] as the approach to implement an IBSC prototype. The QDs are embedded in a host semiconductor material and the electrons, the holes or both of them⁷ are confined in the three space-dimensions. This confinement causes the appearance of discrete energy levels for the electrons and lead to a true zero density of states between the confined states and the host semiconductor, isolating the IB from the VB and the CB. The requirements to achieve an IBSC are determined by the

⁷It depends on the QD-type: In type-I QDs, electrons and holes are both confined in the QD layer; for type-II structures, either the electron or the hole is confined in the dot while the other carrier remains in the barrier material.

material combination, the size and shape of the QDs, which fix the IB position [Faf 99], and by the modulation doping, which provides the half-filling of the IB [Mar 01].

QD technology has been widely investigated in many electronic fields and a majority of IBSCs have been made with this technology. We call it quantum-dot IBSC (QD-IBSC) and we will use along this thesis the notation X/Y for the quantum-dot intermediate band (QD-IB) material, where X is the QD material and Y is the material of the host matrix. QD-IB materials have been grown mainly by molecular beam epitaxy (MBE), based on the controlled deposition of atoms and molecules, or by metalorganic vapour phase epitaxy (MOVPE), based on chemical reactions, also known as metalorganic chemical vapour deposition (MOCVD). The most extended fabrication technique of QD structures by means of MBE is the Stranski-Krastanov (S-K) growth mode, in which QDs are formed to relax the strain caused by the difference in lattice constant between the QD semiconductor and the host semiconductor. Because of being a mature technology, InAs/GaAs QDs were the first candidates used for implementing IBSC prototypes, which allowed the demonstration of the operation principles of QD-IBSC [Mar 06, Lin 12]. However, they do not present an optimum bandgap distribution.

However, QD-IBSCs have also revealed some practical problems. These problems impact the performance of the devices and the achievement of the high theoretical limiting efficiency of IBSCs promises too difficult. Focusing on QD-IBSC devices, the first inconvenience is the weak sub-bandgap absorption involving the confined states in the QDs. This can be explained by two main reasons: a low-volumetric density of QDs and the limited number of QD layers that can be piled during the growth⁸. On the one hand, the low-volumetric density of QDs (in the range of $10^{15} - 10^{16} \text{ cm}^{-3}$) is much lower than the one predicted for optimum QD-IBSC performance and it can be increased by using substrates with higher crystallographical index, which increases the QD areal density [Aka 98, Aka 02], and/or by reducing the thickness of the barriers or

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⁸A high number of QD layers does not intrinsically degrade the performance of the QD-IBSC, it is just that the required time of growth of that high number of QD layers with wide-enough spacers is not a feasible goal.

spacers between QD layers during the growth. Reduction of the QD size⁹ has also been proposed as an alternative to increase sub-bandgap absorptions [Mel 12, Mel 13]. On the other hand, the number of stacked QD layers are limited (typically less than 50 layers) in S-K growth because it results in an excess of accumulated strain in the stacking configuration. This degrades the optoelectronic properties of the material, which leads to a significant non-radiative recombination and a reduction in PC production [Mar 07]. To achieve high stacked QDs layers with no degradation, different growth techniques, like intermittent deposition [Sug 10] and strain-compensation [Osh 10, Hub 10].

Figure 1.7: (a) Simplified band diagram of QD-IBSC with type-I QD. The most relevant energy gaps (E_H , E_{QD} , E_H , E_L , E_{WL} , E_{ES}), some confined states for electrons (GS_e , $ES1_e$, $ES2_e$), and the VBO are indicated. (b) Source mechanisms of voltage reduction in QD-IBSCs. Black arrows depict non-radiative SRH recombination processes: (1) in the host material and (2) in the vicinity of the QD interfaces. Red arrows represent thermal processes: (3) carrier relaxation, and (4) thermal carrier escape. The dashed arrow (5) represents tunnel carrier escape.

The second inconvenience is the excessive voltage degradation of the QD-IBSC with respect to its reference cell (a control solar cell with the same semiconductor structure than the QD-IBSC, but in which the QD-IB material has been replaced by a conventional semiconductor). The excessive voltage drop can be understood with the aid of the

⁹Smaller-size QDs increase both the absorption coefficient of confined states and the QD areal density, but tend to rise the energy of the first confined state.

simplified band diagram of a QD –type-I QD grown by S-K– depicted in Figure 1.7 (a). The QD-region, presenting a bandgap of E_{QD} , is embebed in between the host semiconductor, whose bandgap is E_G . A very thin layer of QD material, called the wetting layer (WL), is formed before the formation of the dots. The WL exhibits a new bandgap, E_{WL} ($E_G > E_{\text{WL}} > E_{\text{QD}}$). For type-I QD, electrons and holes are both confined in the QD layer. Because the effective mass of holes is greater than the one for electrons, the density of confined states for holes is larger than the density of confined states for electrons. On one hand, this results in closely spaced confined states for holes and hence they can be accepted as an extension of the VB of the host material. This fact introduces an energy shift, called valence band offset (VBO), defined as the difference between the top of the VB and the least energetic confined state. On the other hand, the number of confined states for electrons depends on the size and shape of the QDs. As an example, we have depicted three confined states: the ground state, GS_e , and two excited states, ES1_e and ES2_e , respectively. Being GS_e the IB, the two sub-bandgaps induced by it are defined as E_H –for the difference between GS_e and GS_h – and as E_L –for the difference between the bottom of the CB and GS_e –. Analysing the diagram, and as a consequence of the VBO, $E_H + E_L < E_G$ in type-I QDs.

Once the sketch of the band diagram of QD-IBSC with type-I QD has been stated, Figure 1.7 (b) shows mechanisms of voltage reduction in QD-IBSCs. Theoretically, an ideal IBSC works in the radiative limit, but, under one-sun illumination, voltage losses (compared with the reference cell) are produced [Mar 08a] due to the extra recombination paths induced by the IB. In real IBSCs non-radiative SRH and Auger recombination can take place. The non-radiative recombination (NRR) occurs via recombination centers from the QD-growth defects. The extra non-radiative processes are depicted as black arrows in the figure, labeled (1) (taking place in the host material) and (2) (taking place in the vicinity of the QD interfaces). When the IBSC works under high solar concentration, the voltage drop with respect to the reference cell should be negligible in theory. This is due to the fact that as current density increases, the impact of the recombination via the IB on the overall recombination diminishes. Despite that, other degrading processes appear in real QD-IBSCs. Thermal carrier processes are depicted

by red arrows in the figure. Arrows labeled (3) depict carrier thermal relaxation and arrow (4) represents the thermal carrier escape that prevents the QFL-split between the IB and the CB [Ant 10a]. Additionally, tunnel carrier escape from the confined states may also take place in QD-IBSC degrading the performance of the QD-IBSCs by reducing their open-circuit voltage (V_{OC})¹⁰. So far, at room temperature and under one-sun illumination, the V_{OC} of QD-IBSCs has never exceeded the value of E_H divided by e [Ram 14d]. On the other hand, when high concentration factor is used, the V_{OC} can surpass the E_H [Lin 12, Ram 15]. For the case of one-sun illuminated QD-IBSC, recent works have reported QD-IBSC voltage similar to the reference cell voltage [Bai 12].

1.3 State of the art of QD-IBSCs

The final aim of the IBSC is to provide a high-efficiency solar cell. Significant research effort into QD-IBSCs has focus on demonstrating the aforementioned IBSC operating principles. They are (1) the generation of two-photon sub-bandgap PC and (2) the voltage recovery with no limitation due to the IB. The progress of the IBSC has been reviewed in detail in [Ram 14d, Oka 15] and in this section our intention is to summarize the main advances to date in QD-IBSC research.

After the IBSC concept was carried out in 1997, efforts were employed into quantum efficiency measurements for proving the production of sub-bandgap PC in this material system [Luq 04]. It was not until 2006 when the sub-bandgap PC could be measured by the two-photon effect [Mar 06]. The demonstration of this key operating principle of the IBSC was carried out at cryogenic temperatures. Later, cryogenic temperature was also needed for proving the voltage preservation [Ant 10a, Lin 12], which is the second operation principle of the IBSC. They showed that the voltage operation of the cell was not limited by the sub-bandgaps imposed by the inclusion of the IB. Some InAs/GaAs QD solar cells presented minor voltage reduction [Gui 10, Bai 11]. Furthermore, several

¹⁰Open-circuit voltage, V_{OC} , is the voltage measured under particular illumination conditions, when the current flowing through the electrical terminals is zero. Short-circuit current, J_{SC} , is the current measured at short circuit conditions, that is, when the voltage difference between the electrical terminals of the solar cell is zero.

approaches have been carried out to incorporate some elements to the QD layers, like GaP layers [Hub 08], additional layers to the epitaxy, such as GaNAs, or even the inclusion of a small amount of N, P or Sb in the host material [Ant 11]. But, as it was mentioned, the InAs/GaAs prototypes are always limited by the bandgap of the GaAs barriers. All these prototypes were the precursors of better subsequent QD-IBSCs.

Lately, wide-bandgap materials have been proposed to implement QD-IBSCs in which the bandgap of the barrier is larger than the bandgap of the GaAs. Those QD systems are InAs/AlGaAs, GaAs/AlGaAs and InAs/InGaP. They provide a better distribution of the bandgaps, above all, higher E_L , which results in reduced thermal carrier escape [Lin 12, Ram 12]. In addition, InAs/AlGaAs QD-IBSCs have shown the most lately outstanding results: it has been possible to resolve the three optical transitions involved in the operation of IBSCs [Ram 14a, Tam 14]. In [Ram 14a] it has also been proved the "voltage up-conversion" phenomenon, which consists of the production of $V_{OC} > h\nu$ in an IBSC under monochromatic illumination with photons of energy $h\nu < E_G$. This is explained by these photons being absorbed in both E_H and E_L transitions, therefore generating a total $\mu_{CV} = \mu_{CI} + \mu_{IV}$ that is only limited by E_G , and can therefore surpass $h\nu$. Moreover, in this work, both operating principles have been demonstrated in the same device for the first time.

Beyond that, one of the greatest challenges in IBSC has been to prove at room temperature the two operation principles of the IBSC. Recently, this important goal has been reached experimentally (Esther 2016).

Despite the efforts in QD-IBSCs researchs and their advances, we remind again that two main problems still curb the performance of IBSC solar cells: (1) the inefficient sub-bandgap absorption and (2) the excessive voltage degradation of the IBSC compared with the reference solar cell. These problems have been common in almost all IBSC, not only in those based on QDs.

1.4 Scope and outline of the Thesis

The work presented in this Thesis has been carried out at the Silicon and Novel Solar Cells Concepts Group (NSCCG) of the Instituto de Energía Solar (IES) of the Universidad Politécnica de Madrid (UPM). The IBSC concept was proposed within this group in 1997, as it has mentioned above. Along the 20 years that followed, the operation principles of the IBSC have been demonstrated. The main shortcomings which limit the performance of real IBSCs have also been established. In this context, the main objective of this Thesis is to contribute to the development and the enhancement of practical QD-IBSCs. One of the issues of the QD-IBSCs is the poor absorption of the QD for pumping electrons from the IB to the CB and produce PC due to sub-bandgap absorption of photons. Several ideas have been proposed to solve it, from increasing the number of QD layers to the use of light-trapping techniques [Mel 14, Smi 16]. These light-trapping techniques can be incorporated in the fabrication of the IBSC trying to achieved a better behavior of the devices. Moreover, in this Thesis, we extend the understanding of the IBSC theoretical framework by means of the measurement of *two-photon photovoltage* (TPPV), which will be described later on.

In addition, this Thesis contributes to the development of a new processing method of thin-film solar cells compatible with low-temperature characterization, also suitable with the processing of QD-IBSCs, through which, the research capabilities of fabrication of the NSCCG have been expanded. Finally, it seeks to expand the understanding of other high-efficiency solar cell concepts, in particular the MJSCs and multi-terminal solar cells, providing a wider perspective to analyze their efficiency and behavior.

Chapter 2 is devoted to the study of the inclusion of light-trapping techniques in QD-IBSC. We propose the use of texturing the substrate, pursuing the upgrade of the photon absorption in the QDs through light confinement. We have processed and characterized wide-bandgap QD-IBSC samples based on InAs/AlGaAs QDs. We present extensive characterization of the textured InAs/AlGaAs QD-IBSC devices: from morphological measurements, such as profiler measurements and electronic microscope images, to op-

toelectronic characterization, such as EQE ¹¹ and $J - V$ measurements. The textured QD-IBSC samples have shown an improvement in the absorption of sub-bandgap photons. We show from experimental measurements that sub-bandgap photon absorption is increased due to the texturing.

Regarding the topic of IBSC, we extend the characterization of QD-IBSCs in Chapter 3, where we show for the first time the TPPV phenomenon in GaSb/GaAs QD-IBSC prototypes.

In Chapter 4 we present a new substrate removal processing method for III-V solar cells compatible with low-temperature characterization. This is applicable to QD-IBSC based on InAs/AlGaAs materials. Thanks to the implementation of this new processing method, we have added to our facilities a new processing set-up, which includes a vacuum chamber for soldering and a electroplating system for electrolysis-depositing metal contacts. Following this method, we have fabricated and characterized thin-film AlGaAs solar cells. We show the adequacy of this method to measure at low temperatures by measuring the PC or quantum efficiency of the devices at different temperatures.

Chapter 5 contributes to the understanding of other high-efficiency solar cell concepts, in particular, we study the limiting efficiency of the annual energy production of MJSCs, making a comparison between series-connected and independently-connected architectures. The efficiency of photovoltaic conversion for tandem systems is revised. Multi-junction solar cell independently connected (MJSC-IC) have a greater photovoltaic conversion efficiency than Multi-junction solar cell series connected (MJSC-SC). In addition, we also discuss the concept of annual energy production efficiency (AEE) in order to analyze the optimization of the MJSC. Due to the removal of the series connection constrain, MJSC-ICs also show higher AEE than MJSC-SCs for the same number of cells. However, for example, implementing several terminals to a four (or five) junctions MJSC-SC, converting it into a MJSC-IC offers a higher AEE gain than implementing a five (or six) junctions MJSC-SC. Finally, in Chapter 6 we compile

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¹¹ EQE is the external quantum efficiency, which is the ratio of the number of carriers collected by the solar cell to the number of photons of a given energy incident on the solar cell.

the main results and conclusions of the work presented in this Thesis. We also indicate possible future lines of work for which this Thesis opens this path in Chapter 7.

Chapter 2

Implementation of light management approaches in InAs/AlGaAs QD-IB devices

2.1 Introduction

In this chapter, we focus on the study of InAs/AlGaAs QD-IBSCs due to their promising results and advantageous bandgap distribution, as described in Section 1.3. As it was mentioned in Chapter 1, QD-IBSCs present two main shortcomings that prevent them from reaching high conversion efficiencies: (1) the excessive voltage drop with respect to its reference, which was already described and analysed ; and (2) the low sub-bandgap photogenerated current. The low sub-bandgap photocurrent is due to the weak absorption of sub-bandgap photons in the QD stack and the limited number of QD-layers that can be piled. These reasons were explained in Section 1.2. Despite an optimized structure design, QDs absorb weakly in the two sub-bandgap transitions related to the confined states of the QD, that is, E_H and E_L ¹. Consequently, these absorptions must be enhanced to improve the performance of real QD-IBSC devices. Two approaches for increasing absorption are:

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¹See Figure 1.7.

- Increasing the number of QDs in the stack. However, this may degrade the optoelectronic properties of the material due to an accumulated strain excess in the stacking configuration. Also, it is technologically challenging to increase the concentration of QDs by two or three orders of magnitude (see Figure 2.2).
- Incorporating light-trapping structures, such as the optical texturing of the substrate that cause incident photons to be more strongly absorbed in the QD stack due to the increase of the effective optical path.

In this Chapter, we are going to study the application of surface texturing as light-trapping technique with the aim of enhancing the absorption in the E_H and E_L transitions of the QDs.

2.1.1 Light trapping in QD-IBSCs

The photon absorption probability in solar cells depends on the absorptivity of the material and the distance that photons travel in the absorber layer. This photon absorption probability is proportional to the optical path length, which can be defined as $\alpha \times d$, where d is the optical thickness of the absorber layer and α is the absorption coefficient. In state-of-the-art IBSC, this optical path length is large for photons with $E > E_G$ and is very small for photons with $E < E_G$, specially when $E < E_H$. By means light-trapping techniques, optically thick QD-IBSC could be achieved by increasing d .

Light trapping has been used for years as a way to improve absorption in weakly absorbing semiconductor solar cells, such as crystalline silicon [Red 74, Yab 82]. In the framework of geometric optics, structures with randomly textured surfaces have been used for many years for trapping light in solar cells by total reflection in the semiconductor if, at least, one of the surfaces is textured [Yab 82] and randomization of the energy and propagation direction happen inside the solar cell absorbing layers. These randomly textured surfaces lead to an increase of the optical path length. In the low-absorption limit, total randomization of the light (with a proper angular average of the optical path length of oblique light rays) leads to the enhancement of absorption by a

factor of $4n^2$, where n is the semiconductor refractive index. Those light rays scattered with angles beyond the critical angle are totally trapped inside the cell. Indeed, light-trapping approach is also attractive for the III-V semiconductor based solar cells in which nanostructures, such as QDs, are included.

Figure 2.1: Light-trapping scheme on the back surface of a solar cell prototype.

A scheme of light-trapping by means of surface texturing on a solar cell device is depicted in Figure 2.1. Attending to the wavelength of the photons of interest for solar cells (in the range, in most cases, up to one micron), light-trapping textures are mainly divided in two types: (1) sub-micron scale surface roughening (applied to thin-film solar cells), and (2) geometric patterning of the surface with microns-dimension (favoured in bulk c-Si solar cells). Light scattering occurs on the surfaces of these two textures in accordance to geometric-optical phenomena. The aim is to achieve isotropic scattering of the impinging photons inside the absorber layer, which leads to internal reflection in the structure. The limit of completely isotropic scattering (Lambertian limit) carries the mean optical path length enhancement of incident photons to be approximately $4n^2$. This limit is valid for thickness of the absorber of the solar cell much larger than the wavelength of incident photons.

2.1.2 State of the art of light trapping in QD-IBSC

In addition to the early models valid for the very low-absorption limit in silicon solar cells [Goe 81, Yab 82], there were other models developed for higher absorptivity materials, such as III-V semiconductors [Bor 99, Gre 02].

Figure 2.2: Conversion efficiency of QD-IBSCs for different absorption enhancements from the Luque and Mellor's work. Λ_{QD} is the factor by which the number of QDs per unit solar cell area is increased compared to the prototype. Λ_{opt} is the optical path length enhancement achieved by light trapping. The labeled horizontal lines represent values for the single-gap references of that work, Ref.1 and Ref.2 ($E_{G,Ref. 1} = 1.42$ eV and $E_{G,Ref. 2} = 1.24$ eV) and the ideal QD-IBSC. The figure is reprinted from [Mel 14].

For the case of InAs/AlGaAs QD-IBSC, a specific study was carried out in Reference [Mel 14]. The authors could establish that absorption enhancement via light trapping was especially beneficial for InAs/GaAs QD-IBSC prototypes. They proposed (see Figure 2.2) that an optical absorption enhancement (Λ_{opt}) of 10 (being approximately 40 the Lambertian limit) by light-trapping roughening of the rear surface could be enough if it was combined with an increment in the number of QDs layers (Λ_{QD}) by a factor of 30. Without light-trapping techniques Λ_{QD} should be around 800 in order to surpass the efficiency of an equivalent single-gap device.

Some attempts have been carried out by texturing the rear surface of the devices. These approaches have enhanced the absorption in InAs/GaAs epitaxial lift off QD-IBSC devices, demonstrating increase in sub-bandgap absorption by around 30% for photons: $E_G < E < E_H$ [Smi 16]. Textured back surface reflectors on p-GaAs substrates demand an extra photolithographic step. In other work, a self-organized texture has been applied to the semi-insulating (S-I) GaAs substrate of InGaAs/GaAsP multi-quantum-

well solar cells [Wat 15]. This method does not require further photolithographic steps to define the texturing of the surface since it appears as a self-organized pattern (with micron-size pyramids) by means of controlled wet etching. We will follow the latter method, which will be described in depth in Section 2.2.2, in our experimental study of light-trapping in InAs/AlGaAs QD-IB devices by texturing.

2.1.3 IB devices for infrared photodetection: the OTIP

Besides solar cells, QD-IB materials can be employed in other kind of optoelectronic devices, such as a new type of IR detector, called optically triggered infrared photodetector (OTIP), as it was proposed and demonstrated in [Ram 14c].

The OTIP presents the following differences in comparison with conventional semiconductor IR photodetectors: the OTIP is optically triggered and consequently it can be used in optical-communication applications, and it can be operated in short circuit, and therefore, without requiring any voltage supply.

Briefly, the OTIP operates as follow: In short circuit, supra-bandgap light-bias pumps electrons from the VB to the CB and, in absence of IR illumination, some of the electrons circulate through the external circuit and some of them recombine from the CB to the VB, either directly or assisted by the IB. When IR illumination is added, the absorption of these photons pumps electrons from the IB to the CB, reducing the net carrier recombination via the IB. Thus, IR absorption is measured as an increase in photocurrent. So far, it has only been demonstrated operating at low temperature, conditions for which the thermal escape is inhibited.

What we have given here is a brief description of the OTIP theory. For those who pursue a deeper knowledge, the more details can be found in [Ram 14c, Ram 15].

2.1.4 Aim of this chapter

In order to attack the problem of the weak QD absorption, we propose to incorporate self-organized texture on S-I GaAs substrate in an InAs/AlGaAs QD-IBSC. The improvement of light-absorption should be achieved by the enhancement in the photon

absorption by the two sub-bandgap IB transitions (E_H and E_L). Accordingly, we will carry out PC measurements to demonstrate that these QD-IB devices, both IBSCs and OTIPs, can generate extra PC in the two transitions.

For this, we have textured several samples and fabricated a batch of nine different solar cells, whose description is located in Section 2.2. Afterwards, we will provide the morphological and optical results of the textured samples in Section 2.3, and the morphological and optoelectronic characterization of the devices in Section 2.4 and Section 2.5, respectively. Finally, in Section 2.6 we will analyse and discuss the consequences of these experimental results, providing their conclusions in Section 2.7.

2.2 Fabrication of the devices

The study of the application of light-trapping techniques to QD-IBSCs has been carried out in a two-step process. Firstly, we have tested the texturing of S-I GaAs (described in the previous section) on double-polished S-I GaAs wafers. Secondly, we have applied this self-organized texturing of GaAs to the QD-IBSCs structures used in this chapter. The epitaxial structure of the solar cells were grown on S-I GaAs wafers for the QD-IBSC samples since S-I GaAs does not absorb photons with energy lower than the bandgap².

Furthermore, as it was explained in Section 2.1, the benefits of light-trapping can be achieved through total internal reflection by means of the incidence of light on textured surfaces from the media with the highest refractive index into the one with the lowest. Due to the high difference between the refractive index of GaAs and air, it may result in a better approach than the implementation of a reflector, if it is not ideal. In our case, the reflector was a layer of evaporated gold.

For these reasons, we proposed a set of three different approaches to study light-trapping on QD-IBSC structures. These approaches are represented in Figure 2.3. All the samples share the same solar cell structure grown onto S-I GaAs substrate. The

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²The epitaxial structures were fabricated by the Instituto de Microelectrónica de Madrid (CSIC) (IMM).

differences among the three approaches lie on the rear side of the substrate, which were:

- (i) non-textured substrate followed by air, (ii) textured substrate followed by air, and
- (iii) textured substrate followed by back reflector.

Figure 2.3: Sketch of the three texturing approaches employed for the study of light-trapping in QD-IBSC.

This section is devoted to describe the samples and the processes that have been employed to fabricate the QD-IBSCs.

2.2.1 Texturing of S-I GaAs substrates

The first step in our study is to test texturing in S-I GaAs wafers. To this purpose, we divided a double-polished S-I GaAs wafer into three pieces. A wet chemical etching based on NH_4OH was used for texturing these samples. The wet chemical etching consisted in $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:4:80). This etching provides a self-organized randomly-assembled diamond shape due to the anisotropic etching rates depending on the crystal orientation.

The rate of this wet chemical etching depends on its composition, temperature, etching time, and environmental conditions. We have tested different etching times on the

Figure 2.4: Pictures taken with an optical microscope of the self-organized textured GaAs samples. Images (a), (c), and (e) depict GaAs samples that have been etched for different times: 10, 20, and 30 minutes. Each picture shows two differentiated areas: the upper one is the original polished surface of the S-I GaAs wafer and the bottom one the etched area. Images (b), (d), and (f) show a zoom of the etched areas corresponding to each of the etching times.

S-I GaAs in order to achieve different micronmeter scale of the diamond shapes. Pictures of these tests, which were taken with an optical microscope at different magnifications, are shown in Figure 2.4. The images of the left column (a), (c), and (e) show a two-zone picture of the textured S-I GaAs samples. The upper part of each image shows the original polished surface. This surface was covered with photoresist during the wet chemical etching. The lower part of these images shows the etched surface. The texture causes the reflection of light at the etched samples to be lower than the one at the polished surface and, therefore, the etched area appears darker than the polished area. Images at the right column of Figure 2.4 [(b), (d), and (f)] show a zoom of the textured area of the corresponding picture at the left column. The self-organized texture is appreciated in these amplified images. Later on, in Section 2.3 we will provide morphological and optical measurements of these self-organized textured GaAs samples.

2.2.2 Textured QD-IBSC

2.2.2.1 Description of the samples

The structures used in this work have been grown by MBE at the IMM. They consist of AlGaAs p-i-n epitaxial solar-cell structures grown on S-I GaAs wafers, and are depicted in Figure 2.5 (the drawing is not to scale). We will designate the samples as Reference Sample, $10\times$ QD-layers Sample, and $1\times$ QD-layer Sample. The three solar cells have the same structure, except for the QD/bulk region. The difference between the samples are a bulk region of 300-nm undoped AlGaAs in the Reference Sample, a one layer of InAs QDs which is present in the $1\times$ QD-layer Sample, and 10-layers stack of InAs QDs which are present in the $10\times$ QD-layer Sample.

The samples exhibit an upright structure designed to support both metal contacts on the frontside. The device structure were grown each by MBE onto a 3" undoped (001) S-I GaAs wafer. The structure is designed as to withstand n-contact annealing. For this reason a 1000 nm buffer and n-type contact layer ($5\times 10^{18} \text{ cm}^{-3}$) GaAs were grown on the S-I GaAs wafer. Following this buffer and contact layer, a 100 nm n+ ($5\times 10^{18} \text{ cm}^{-3}$) back surface field (BSF) layer with 41 % Al was grown to keep minority electrons

S1: Reference	S2: Optically thin 1-QD layer	S3: Optically thin 10-QD layers	
300 nm p+ GaAs 1×10^{19}	300 nm p+ GaAs 1×10^{19}	300 nm p+ GaAs 1×10^{19}	Contact
5 nm p+ AlAs 5×10^{18}	5 nm p+ AlAs 5×10^{18}	5 nm p+ AlAs 5×10^{18}	SEL
5 nm p+ GaAs 5×10^{18}	5 nm p+ GaAs 5×10^{18}	5 nm p+ GaAs 5×10^{18}	SEL
30 nm p+ $\text{Al}_{0.78}\text{Ga}_{0.22}\text{As}$ 5×10^{18}	30 nm p+ $\text{Al}_{0.78}\text{Ga}_{0.22}\text{As}$ 5×10^{18}	30 nm p+ $\text{Al}_{0.78}\text{Ga}_{0.22}\text{As}$ 5×10^{18}	Window
200 nm p+ $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 1×10^{18}	200 nm p+ $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 1×10^{18}	200 nm p+ $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 1×10^{18}	Emitter
100 nm n $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 3×10^{16}	100 nm n $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 3×10^{16}	100 nm n $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 3×10^{16}	FDL
300 nm un $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ bulk Si δ -dop $3 \times 10^{10} \text{ cm}^{-2}$ 300 nm un $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$	300 nm un $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 1xInAs QD Si δ -dop $3 \times 10^{10} \text{ cm}^{-2}$ 300 nm un $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$	75 nm un $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 10xInAs QD (9x50 nm spacers) Si δ -dop $3 \times 10^{10} \text{ cm}^{-2}$ 75 nm un $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$	QD region / Bulk region
200 nm n+ $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 5×10^{17}	200 nm n+ $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 5×10^{17}	200 nm n+ $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ 5×10^{17}	Base
100 nm n+ $\text{Al}_{0.41}\text{Ga}_{0.59}\text{As}$ 5×10^{18}	100 nm n+ $\text{Al}_{0.41}\text{Ga}_{0.59}\text{As}$ 5×10^{18}	100 nm n+ $\text{Al}_{0.41}\text{Ga}_{0.59}\text{As}$ 5×10^{18}	BSF
1000 nm n-GaAs 5×10^{18}	1000 nm n-GaAs 5×10^{18}	1000 nm n-GaAs 5×10^{18}	Buffer & Contact
SI-GaAs Substrate	SI-GaAs Substrate	SI-GaAs Substrate	

Figure 2.5: The three solar cell structures proposed to study light trapping in QD-IBSC. The three samples are designated as Reference Sample, 1×QD-layer Sample, and 10×QD-layers Sample. The three solar cell structures are identical except for the QD/bulk region. This difference is highlighted with a red, dashed rectangle. A 300-nm-thick bulk region of undoped $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ is included in the Reference Sample and the 1xQD-layer Sample. One layer of InAs QDs was grown embedded in this undoped layer in the 1×QD-layer Sample. For the case of the 10×QD-layers Sample, 10 layers of InAs QDs (separated by 50-nm spacers between each pair of QD layers) were grown embedded in a 150-nm-thick undoped $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$.

away from the back side contact. A 200-nm-thick Si-doped base was then grown. This base is doped to $5 \times 10^{17} \text{ cm}^{-3}$ with 35 % Al. A 600-nm-thick AlGaAs intrinsic layer was grown between the emitter and the base for the cases of the Reference Sample and the 1×QD-layer Sample. For the case of the 1×QD-layer Sample, one layer of InAs QDs was grown embedded in this undoped layer. The QDs were self-assembled after the deposition of two monolayers of InAs. Slab doping with silicon was employed so as to dope the dots with approximately one electron per dot, assuming a QD areal density of $3 \times 10^{10} \text{ cm}^{-2}$. For the case of the 10×QD-layers Sample, 10 layers of the same type of InAs QDs were grown with 50-nm spacers between them and they were embedded in a 150-nm-thick undoped layer. Before a 200-nm-thick Be-doped emitter doped to

$1 \times 10^{18} \text{ cm}^{-3}$, a field-damping layer (FDL)³ of 100-nm n-type ($3 \times 10^{16} \text{ cm}^{-3}$) with 35 % Al was grown. The last layer grown is a 300 nm thick n++ type ($1 \times 10^{19} \text{ cm}^{-3}$) GaAs contact layer. To avoid parasitic absorption in the contact layer –which does not contribute to PC generation–, this has to be selectively etched, using the metal grid as a mask. In order to prevent subsequent layers to be etched, a 5-nm AlAs stop etching layer (SEL) is necessary to protect the rest of the epitaxy. Immediately after contact-layer removal, AlAs-SEL itself is etched in diluted HF. Below it, a 5-nm GaAs layer is left as protection against oxidation in air of the window layer. The total thickness of the active epitaxial layers is 2.5 μm .

Since the substrate is S-I GaAs and the buffer layer is n-GaAs, the light-trapping effect will only have effect on photons $\varepsilon < E_{\text{G,n-GaAs}}$.

2.2.2.2 Fabrication process of textured InAs/AlGaAs QD-IBSC prototypes

The application of the three different texturing approaches to each one of the three solar cell structures under study results in a batch of nine samples.

The first step in the fabrication process of the textured devices is to create the self-organized texture by wet-chemical etching to the back of the solar cells. The back-side texture of the samples was made with the same $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:4:80) etching, tested before on wafer, by covering the front-side wafer (with the epitaxial layers) with photoresist, which prevents the NH_4OH -based etching. A gold coating was deposited by thermal evaporation atop one piece of some textured samples in order to act as back reflector. After that, the final devices of the nine samples are processed on the active epitaxial layers by means of standard photolithography, chemical etching, and thermal evaporation techniques. The metal contacts of the solar cells are AuGe/Ni/Au for the n-type contact (this n-type contact is annealed by rapid thermal annealing) and Cr/Au for the p-type contact.

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³A FDL consists of an n-type (in this case) layer that is inserted in-between the p-emitter and the QD region. The purpose of the FDL is to sustain most of the junction build-in potential so that the QDs can be driven to a flat-band potential region.

Figure 2.6: Mounting of the processed devices. A processed solar cell and a copper disc in which this device is going to be mounted are depicted in (a). A drilled hole on the Cu disc is shown in (b). This hole ensures that behind the mounted device there is air, so that, the reflection of light on the back surface produces the required light trapping. Image (c) depicts the solar cell placed onto the Cu disc soldered by means of spreaded indium as well as the PCB for external connections.

Finally, each individual device is placed on a copper disc, using indium as solder, for external connection and low-temperature measurements. We have drilled the copper discs for placing the samples in such a position that ensures that underneath the solar cell there is air. A sketch of this process is depicted in Figure 2.6. The reason for this is that we want to avoid the reflection of light by the tandem indium-copper disc. In such a way, the light trapping is only due to the reflection on the rear textured surface of the solar cells.

The last step for external connection consists of wire bonding the solar cells. In this respect, thin gold wires (25- μm diameter) connect the front metal grid and the back path contact of the devices to an external printed circuit board (PCB) by wedge wire-bonding. For external connection, thicker copper external wires were soldered with tin to the PCB.

Table 2.1 summarizes the batch of nine solar cells and their assigned names. Following the fabrication process described above, we have processed the samples required in our work to study light-trapping on InAs/AlGaAs QD-IBSCs.

Table 2.1: Summary of the batch of nine InAs/AlGaAs QD-IBSCs.

Approach \ Structure	Reference	1×QD-layer	10×QD-layers
polished+air	Reference polished	1×QD-layer polished	10×QD-layers polished
textured+air	Reference textured+air	1×QD-layer textured+air	10×QD-layers textured+air
textured+gold	Reference textured+gold	1×QD-layer textured+gold	10×QD-layers textured+gold

(a)

(b)

(c)

(d)

Figure 2.7: Some pictures of the processed solar cells. A whole piece of a processed sample is shown in (a). Image (b) is a picture that is taken with an optical microscope of an individual solar cell. This individual device is mounted onto a Cu disc, as it is shown in (c). The main elements of each InAs/AlGaAs QD-IBSC are indicated in these images. A sketch of the solar cell mounted onto the Cu disc with the hole is depicted in (d).

As an example of the fabricated devices, Figure 2.7 shows pictures of a completed solar-cell prototype. Figure 2.7 (a) depicts the whole piece of a processed sample, from which each individual cell is extracted. A picture of an individual solar cell is shown in Figure 2.7 (b) taken at an optical microscope. The main components integrating the InAs/AlGaAs QD-IBSCs are indicated.

The front contact is a p-type Cr/Au metal grid, that covers an area of 0.97 mm^2 . A trench on the epitaxy is done by chemical etching in order to reach the buffer and contact GaAs layer (see Figure 2.3). The back contact is a n-type AuGe/Ni/Au path (0.29 mm^2 of cover area) placed on the buffer GaAs layer. The element which delimits the area of the device and isolates it from the rest of the sample is a mesa. The mesa is a narrow trench of several-micron depth on the epitaxy. The total area of the solar cells is 2.76 mm^2 with a 65 % shading factor. These values are taken from the digital design of the photolithographic masks.

Finally, the individual solar cells are mounted onto a Cu disc. This step is illustrated in Figure 2.7 (c). The elements described before (the solar cell, the Cu disc, the PCBs, the thin-gold wires, and the thicker external wires) are labelled. A sketch of the solar cell mounted onto the Cu disc with the hole is depicted in Figure 2.7 (d).

2.3 Characterization of textured S-I GaAs substrates

We have divided the characterization of the samples in two blocks. Firstly, in this section we present the results from the experimental characterization of the tests on the S-I bare GaAs wafers. We provide morphological and optical characterizations. Secondly, the next two sections are devoted to present the results obtained from the characterization of the textured InAs/AlGaAs QD-IBSCs.

Figure 2.8: SEM images from the textured S-I GaAs substrates. The images at the left column (a), (c), (e) were acquired at a 10000 $\times$ magnification to obtain a general overview of the textured sample surface and the images at the right column (b), (d), (f) were acquired at a 50000 $\times$ magnification to focus on the details of the pyramidal patterns that have been obtained by the self-organized texture wet etching using different times. The mean value of the height (measured with the profiler) of these pyramids is indicated in each image.

2.3.1 Morphological measurements

In addition to the images in Figure 2.4 taken with the optical microscope described in section 2.2.1, we have characterized the textured GaAs substrates by profiler measurements and Scanning Electron Microscope (SEM).

SEM images were acquired by the Institute of Nanoscience of Aragon (INA) at the University of Zaragoza (Spain). The microscope was a SEM Inspect™ F50 operated at 5 keV and different magnifications. The SEM images from the S-I GaAs-substrate samples that have been etched during different times are shown in Figure 2.8.

The profile measurements were acquired with a Profiler AlphaStep DS120. The profiler allows to quickly obtain reliable measurements of shapes and sinkholes on surfaces. Thus, the height of the pyramidal pattern from the self-organized texture was measured by the profiler. The mean value of the pyramide height of the self-organized texture of the GaAs samples is indicated in the SEM images in Figure 2.8, where images (a), (c), and (e) illustrate a general view of the sample surfaces and images (b), (d), and (f) depict a zoom view.

The SEM images of Figure 2.8 (a) and (b) show that the self-organized textured has begun, but the diamond shapes are isolated among them and they are smaller than the micron-size pyramides required. The SEM images of Figure 2.8 (c)-(f) show the sample surfaces completely covered by the self-organized texture. The size of the pyramidal structures are in the micron-range, as required, and their heights are from 300 nm to 500 nm as average.

The time required to etch the final device samples was estimated from these profile measurements and the pictures taken at the optical microscope.

2.3.2 Optical characterization

The goal of light-trapping through self-organized texturing of the rear surface is to achieve internal reflection of the incident light. We intend to characterize optically the textured samples by means of measuring the transmittance of sub-bandgap photons through the sample. The sub-bandgap photons are not absorbed in the S-I GaAs bulk

semiconductor substrate. In the optic framework, the sum of absorbance, reflectance and transmittance has to equal one. So that, if the internal reflection of impinging photons on the textured rear surface increases, the transmittance decreases since the absorbance must be negligible.

We have characterized the S-I GaAs samples by means of measuring the total transmittance, defined by:

$$T(\%) = \frac{I_1}{I_2} \times 100 \quad (2.1)$$

where I_1 is the light intensity transmitted by the sample and I_2 is the light intensity impinging on the sample.

Instead of reporting the results of the absolute transmittance, we will report the relative transmittance, defined

$$T_{\text{relative}}(\%) = \frac{T_{\text{textured}}}{T_{\text{polished}}} \times 100 \quad (2.2)$$

where T_{textured} is the transmittance of the textured S-I GaAs samples and T_{polished} is the transmittance of a polished S-I GaAs sample taken as reference. With this approach, we can compare the reduction of the transmitted light due to the textured surface. Also, the magnitude T_{relative} allows to minimize the effect of possible systematic errors in the measurements.

We have measured the transmittance of the sample using the set-up depicted in Figure 2.9 (a). This set-up consists of the following elements:

- a high-power tungsten light source (360-2400 nm)⁴ from OceanOptics HL-2000™ (from now on the “halogen lamp”).
- Thorlabs™ IS200-4 - Ø2" Integrating Sphere, from now on the “integrating sphere”.
- Spectrometers:
  - OceanOptics™ MAYA 2000PRO (199-1102 nm) for the visible/near-infrared range (VIS/NIR).

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⁴The color temperature associated with the light power is 2800 K.

- OceanOptics™ NIRQUEST (900-2200 nm) for the near-infrared range (NIR).
- two kind of optic fibers:
  - OceanOptics™ VIS-NIR/UV-VIS Y-shape fiber of 600- μm diameter.
  - OceanOptics™ NIR fiber of 600- μm diameter.

Figure 2.9: Set-up (a) to measure the transmittance of the textured GaAs samples. The relative transmittance of the textured GaAs samples for two energy ranges of light are shown in plots (b) and (c). Plot (d) shows the transmittance obtained using FTIR spectroscopy.

The halogen lamp is placed next to the integrating sphere, ensuring that the output light from the lamp impinges on the input port of the integrating sphere. The fiber connector is placed on the detector port to connect the integrating sphere and the spectrometer. The measurement is registered and recorded by means of the OceanView software.

The transmittance is measured in a two-step process: firstly, the reference spectra of the halogen lamp is acquired and secondly, the sample is placed (with the polished side faced the lamp) on the input port (being sure that the sample is covering the 2"-port), so that it is interposed between the halogen lamp and the integrating sphere.

As mentioned, the input port of the integrating sphere has a diameter of 2", whereby the textured GaAs samples must be at least squares with sides of 2". In this respect, we could not measure the transmittance of the actual textured S-I GaAs samples described in Section 2.3.1 since they were smaller than the required 2"-size. Instead we fabricated larger textured S-I GaAs samples using the self-organized wet chemical etching based on NH_4OH described in Section 2.2.1.

We have related the height of the diamond pattern to the relative transmittance, as depicted in Figure 2.9 (b) and (c) for the VIS/NIR and NIR ranges, respectively. In these graphs, the measurement from the polished GaAs sample is scaled as a reference characterized by a 100 % transmittance. The relative transmittance measurements from two textured S-I GaAs samples are shown in different colors. The higher the motives of the textured samples are, the smaller the relative transmittance is. As a complement, the normal transmittance⁵ measured by FTIR⁶ of a polished GaAs wafer is depicted in Figure 2.9. As it is known, the transmittance of intrinsic GaAs wafers is approximately 50 % in the near-middle infrared (IR) range. These results show that the self-organized texturing of S-I GaAs samples works and it increases the internal reflection of incident light.

2.4 Morphological characterization of textured QD-IBSCs

The results from the measurements of the textured InAs/AlGaAs QD-IBSCs are divided in two separated sections. This section is devoted to report on the morphological char-

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⁵The normal transmittance is measured at 0° of input and output light.

⁶The Fourier Transform Infrared spectroscopy measures absorption, transmission, reflection or emission of materials in a wide infrared spectrum.

acterization of the textured QD-IBSCs and the following section will report on their optoelectronic characterization.

The morphological characterization of the textured QD-IBSCs consists of SEM and transmission electron microscopy (TEM) images. The SEM images were acquired using the same microscope described in section 2.3.1. The TEM images were also acquired at the Institute of Nanoscience of Aragon (INA). TEM and Selected Area Electron Diffraction (SAED) were performed to determine the morphology and structure of the materials, whereas Scanning-TEM (STEM) was performed to determine the composition of the samples. Both techniques were carried out in a Tecnai F30 microscope (FEI Company) at a working voltage of 300 KV. TEM images were obtained with a coupled charge-coupled device camera (Gatan). The Fast Fourier Transform (FFT) of several high resolution TEM images was also used in order to analyze the crystalline structure of the samples. Regarding the STEM, STEM-High Angle Annular Dark Field (STEM-HAADF) images were obtained with a HAADF detector (Fischione). In this mode, the intensity of the signal is proportional to the square of the atomic number, therefore, heavier elements appear with a much brighter contrast than lighter elements, like carbon or silicon. Also, in order to analyze the chemical composition of the materials, X-ray Energy Dispersive Spectra (EDS) data were obtained with an EDAX detector.

2.4.1 SEM measurements of the textured QD-IBSCs

Figure 2.10 depicts the SEM images of the rear side of the $1\times$ QD-layer Sample ((a) and (b)) and $10\times$ QD-layers Sample ((c) and (d)). These surfaces were etched using the self-organized wet chemical etching $-\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:4:80)–. The etching depends on environment conditions, such as temperature, power of exhaust hood, etc., thus the etching rate was variable. Therefore, to ensure reproducibility, the final texture was achieved by means of double checking the roughness and the reflection of the surface at the optical microscope by comparison with the S-I GaAs samples presented in Section 2.2.1. The self-organized textures of both samples appear to be homogeneously distributed along the surface. Moreover, in both samples, the size of the diamond-shape

pattern is in the micron-range. The height, that has been measured by profiler, is approximately 400 nm.

Figure 2.10: SEM images from the rear side of the textured $1\times$ QD-layer Sample ((a) and (b)) and textured $10\times$ QD-layers Sample ((c) and (d)), which were made using the self-organized wet chemical etching based on NH_4OH described in Section 2.2.1. The images (a) and (c) were acquired using $10000\times$ magnification in order to obtain a general overview of the textured surfaces. The images (b) and (d) were acquired at a $50000\times$ magnification to focus on the details of the pyramidal patterns that have been obtained by the self-organized texture wet etching.

2.4.2 TEM measurements of the QD-IBSC structures

The QD-IBSC structures ($1\times$ QD-layer Sample and $10\times$ QD-layers Sample) grown by MBE have been characterized by the two kinds of TEM measurements described above. Samples for TEM measurements need to be slimmed down using electron bombardment. Although this process can potentially damage the samples, STEM images did not reveal any damage on the TEM samples.

2.4.2.1 $1\times$ QD-layer Sample

Figure 2.11 depicts some High-resolution TEM (HRTEM) images from the $1\times$ QD-layer Sample. TEM samples were mounted at a holder facing two pieces of the same sample, as shown in Figure 2.11 (a) (where the surfaces of these samples are highlighted with a purple arrow). The direction of growth of the epitaxy is indicated by a yellow arrow. In addition, the epitaxial layers are indicated with a pink arrow. Finally, the InAs QD layer is flagged with a red rectangle. This image shows a general view of the epitaxy.

In Figure 2.11 (b), the InAs QD layer is also highlighted with a red rectangle and the QDs can now be appreciated. In this image, structural defects become apparent. These defects are magnified in Figure 2.11 (c). The growth of the QDs generates strain in the epitaxy. This is likely cause of the dislocations. InAs QDs have a lentil-shape with an approximately 10-nm height and a 20-nm basis.

Figure 2.12 shows STEM images of the $1\times$ QD-layer Sample. The direction of growth is labeled by a blue arrow in (a). In this image, the epitaxial layers, which are indicated by a pink arrow in Figure 2.12, can be seen because the STEM technique reveals differences in the material composition. Figure 2.12 depicts a magnified picture of the InAs QDs layer. As well as in Figure 2.11, the InAs QD layer is highlighted by a red rectangle. Furthermore, we point out that the nanometric-width WL wetting layer that is formed in a QD-epitaxy growth is easily appreciated in these images.

As it was mentioned before, STEM measurements can be used also for analytical techniques and spectroscopic mapping. Figure 2.13 is a composed image combining a STEM image of the QD layer (upper side) with the corresponding an Energy Dispersive

X-ray (EDX) spectroscopy of a single QD. The analysis (bottom side of Figure 2.13) shows the InAs composition of the QD, however, Ga appears in the spectrum maybe due to diffusion into the QD from the GaAs host.

Figure 2.11: HRTEM images of the 1xQD-layer Sample. Image (a) depicts two-faced samples where the direction of growth is indicated by a yellow arrow. This is also indicated in (b). The QD layer is flagged in images (a), (b), and (c). Images (b) and (c) reveal structural defects of the structures. Image (d) shows some of the InAs QDs from the layer.

Figure 2.12: STEM images of the $1 \times$ QD-layer Sample. In image (a) the epitaxial layers can be seen and they are indicated by a pink arrow. The direction of growth is flagged by a blue arrow and the QDs layer is remarked by a red rectangle. Image (b) is a zoom of the QD-layer area.

Figure 2.13: STEM image (up) of the QD-layer area from the $1 \times$ QD-layer Sample and the EDX spectroscopy (down) of the QD.

2.4.2.2 10×QD-layers Sample

Figure 2.14 depicts some HRTEM images from the 10×QD-layer Sample. Figure 2.14 (a) show the epitaxial layers. The direction of growth of the epitaxy is indicated with a yellow arrow. The QDs layers are flagged with a red rectangle. This image gives a general view of this area of the epitaxy.

Figure 2.14 (b) depicts an amplified image of the QD layer area. In this image, many structural defects become apparent. These defects are highlighted by green circles. As it was explained before, although the growth of the QDs can generate strain in the structure, this stress should be relaxed through the spacers between each pair of QD layer. However, the strain in the structure in the samples has not relaxed and several dislocations are formed. Furthermore, these dislocations have caused that the InAs QDs had not formed properly along the layers. The formed InAs QDs have a lentil-shape with a approximately 10-nm height and a 20-nm basis, as it can be seen in Figure 2.14 (c). Finally, Figure 2.14 (d) depicts one of the dislocations. As well as in the HRTEM images from the 1×QD-layer sample, the WL is also appreciated in the images of the 10×QD-layer sample.

Figure 2.15 shows STEM images of the 10×QD-layers Sample. The direction of growth is labeled by a blue arrow in (a). The epitaxial layers are indicated by a pink arrow in Figure 2.15. Figure 2.15 shows a zoomed picture of the InAs QDs layer. As well as in Figure 2.14, the InAs QD layer is highlighted by a red rectangle.

Figure 2.16 is a composed image where a STEM image of the 10×QD-layers stack (left-upper side) has been employed for the EDX spectroscopy of a transversal path of QD. The analysis (right-upper and bottom sides of Figure 2.16) shows the InAs composition of the QD. However, Ga appears in this analysis, maybe due to diffusion into the QD from the GaAs host.

Figure 2.14: HRTEM images of the 10 $\times$ QD-layer Sample. Image (a) mainly depicts the 10 QDs layers and following epitaxial layers of the sample. The yellow arrow indicates the direction of growth. The red rectangle flags the 10 $\times$ QD-layers. Many defects are present in this structure, as it can be seen in (a) and (b), in which they are highlighted by green circles. Images (c) and (d) show an InAs QD and a dislocation, respectively.

Figure 2.15: STEM images of the 10 $\times$ QD-layer Sample. In image (a) the epitaxial layers can be seen and they are indicated by a pink arrow. The direction of growth is labeled with a blue arrow and the QDs layer is remarked by a red rectangle. Image (b) is a zoom from the QD-layer area.

Figure 2.16: STEM image (left-up) of the QD-layers from the 10 $\times$ QD-layer Sample area and corresponding EDX spectroscopy (right-up and down) of the QD.

2.5 Optoelectronic characterization of textured QD-IBSCs

2.5.1 Quantum efficiency at room temperature

External Quantum Efficiency (EQE) and PC measurements at room temperature were done with the set-up depicted in Figure 2.17. The beam light from an OSRAM 100 W HLX halogen light bulb was chopped and diffracted with the aid of a Cornerstone 260™ 1/4 m monochromator M-74100 Newport®. The PC detection was done using conventional lock-in techniques (Stanford Research Systems® DSP Lock-in Amplifier, Model SR830) to measure at the chopping frequency and a low-noise transimpedance preamplifier (Stanford Research Systems®, Model SR570). This amplifier also served as voltage source to bias the sample. All measurements were performed at zero voltage bias.

Figure 2.17: Set-up to measure the EQE of the solar cells at room temperature.

Figure 2.18 shows the EQE of the batch of nine samples as a function of the photon excitation energy at room temperature. The three sets of solar cells are identified by different families of colors. The *EQE* goes from values from above 0.1, corresponding to the supra-bandgap $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ (whose theoretical bangap is indicated with dashed line on the graph) response to 10^{-5} , corresponding to noise level. Besides, the theoretical bandgap of the buffer layer (n-GaAs) is also indicated by a dashed line on the graph.

For the cases of $1\times$ QD-layer and $10\times$ QD-layers samples, sub-bandgap response can also be measured at 300 K. This response is attributed to the absorption of light in the InAs-QD region.

Figure 2.18: *EQE* measurement of the batch of nine samples as a function of the photon excitation energy at room temperature. The three sets of solar cells are identified by different colors. The reddish *EQE* characteristic are from the $10\times$ QD-layers samples (textured+gold, textures+air, polished+air). The bluish ones are from the $1\times$ QD-layer samples. The greenish ones are from the Reference samples. The theoretical bandgaps of $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ and n-GaAs at room temperature are indicated with dashed lines.

The highest *EQE* values correspond to the Reference Samples. Although the Al-GaAs layer structure of this Reference samples did not include any QD layer, there is, though, PC generated for sub-bandgap energies. The threshold of this response disappears at the n-GaAs bandgap. We speculate in this respect that the n-GaAs buffer layer is contributing to the *EQE* response. The relatively low values of the supra-bandgap *EQE* of the batch of nine samples is due to the non-optimized solar cell layer structure,

the lack of anti-reflective coating, and, for the cases of $1\times$ QD-layer and $10\times$ QD-layers samples, increased carrier recombination introduced by the QDs. Moreover, carrier recombination may result from the structural defects, that the epitaxial structures exhibit (see TEM and STEM Figures 2.11 - Figure 2.16). In addition, the *EQE* both supra-bandgap and sub-bandgap values for the $10\times$ QD-layers Samples are lower than the ones for $1\times$ QD-layer Samples.

Figure 2.19: *EQE* measurement of the $1\times$ QD-layer samples (textured+gold, textured+air, polished+air) as a function of the photon excitation energy and at room temperature. Sub-bandgap n-GaAs EQEs of the $1\times$ QD-layer samples are superimposed on the left side of the graph in linear scale. The J_{SC} values obtained from the integration of the *EQE* for each sample are summarized in the chart at the bottom of the graph.

In Figures 2.19 and 2.20 we have depicted separately the *EQE* of the $1\times$ QD-layer samples and $10\times$ QD-layers samples, respectively. In both cases, there are three samples of solar cells for each structure: textured+gold, textured+air and polished+air. These graphs allow a better understanding of the measurement of each set of samples. The *EQE* responses for sub-bandgap transitions have been magnified in an inset graph in linear scale (from the n-GaAs bandgap, 1.42 eV, to 1 eV), they are designed as sub-bandgap n-GaAs EQE. Furthermore, the J_{SC} values, obtained by integration of the *EQE* are included in an inset table. Three different values of J_{SC} are given: the total J_{SC}

obtained from the integration of the EQE along all the spectral range, the sub-AlGaAs J_{SC} , obtained through the integration of the EQE for energies below the $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ bandgap, and the sub-GaAs J_{SC} , obtained by integrating EQE for energies below the n-GaAs bandgap. From these values, we can compare the contribution of sub-bandgap transitions to the J_{SC} of the textured InAs/AlGaAs QD-IBSCs.

Figure 2.20: EQE measurement of the $10\times QD$ -layers samples (textured+gold, textured+air, polished+air) as a function of the photon excitation energy and at room temperature. Sub-bandgap n-GaAs $EQEs$ of the $10\times QD$ -layers samples are superimposed on the left side of the graph in linear scale. The J_{SC} values obtained from the integration of the EQE for each sample are summarized in the chart at the bottom of the graph.

2.5.2 Current-density characteristic

Current-voltage ($J - V$) measurements were performed under approximated AM1.5D solar spectrum illumination and standard measurement conditions. The spectrum was obtained by filtering light from a xenon lamp light with appropriate AM1.5D filters. In the same measurements, a GaAs wafer (acting as an optical filter) was placed later in-between the solar simulator and the samples to measure the direct contribution of GaAs

sub-bandgap transitions. The distance between the solar simulator, GaAs wafer, and different samples was kept constant along the measurements.

Figure 2.21: Current density-Voltage characteristic at room temperature of the batch of nine samples. The measurements were performed under approximated AM1.5D solar spectrum and standard measurement conditions. The three sets of solar cells are identified by different colors. The reddish $J - V$ characteristic are from the samples with 10 layers of QDs. The bluish ones are from the samples with 1 layer of QDs. The greenish ones are from the reference samples.

The room temperature $J - V$ characteristics for the batch of samples are shown in Figure 2.21. To measure the $J - V$ characteristic devices were placed setting the height of the solar spectrum in such a way that the J_{SC} of the Reference polished+air Sample would be the same than the integrated value obtained from the EQE response. In these figures, we have preserved the same color legend than the one used when plotting the EQE . The $J - V$ characteristic with the highest J_{SC} and V_{OC} of the batch of devices correspond to the Reference samples (Figure 2.21 greenish curves). Consistently with the EQE response, the 10×QD-layers samples exhibit the lowest $J - V$ response (Figure 2.21 reddish curves). These $J - V$ characteristics demonstrate that the InAs/AlGaAs

QD-IBSCs are operational. However, the $J - V$ characteristic of the $1 \times \text{QD}$ -layers and $10 \times \text{QD}$ -layers Samples are affected by recombination processes induced by the quality of the QD stack and the amount of dislocations in the structure (see figures 2.11 and 2.14).

Figure 2.22: Sub-GaAs current density-voltage characteristics at room temperature of the batch of samples. The measurements were performed under the same solar spectrum and standard conditions than the total $J - V$. A n-type GaAs wafer, acting as a filter was located in-between the solar simulator and the samples. The color legend show the $J - V$ curves plotted with the same color legend than the one used in Figure 2.21.

As well as in the EQE measurements, one of the most interesting points of the QD-IBSC response relies on the sub-bandgap response of the solar cells. To this end, we have measured the $J - V$ characteristics while placing a GaAs wafer in-between the solar simulator and the samples in order to filter supra-bandgap energy photons. By doing so, we can study the contribution of sub-bandgap transitions to the $J - V$ characteristics of the QD-IBSCs. When analyzing the n-GaAs sub-bandgap contribution to the $J - V$ response of the solar cells in Figure 2.22 we find that, while the Reference samples do

Table 2.2: V_{OC} and J_{SC} of the QD-IBSCs studied in this work under approximate AM1.5D solar spectrum and standard measurement conditions.

	V_{OC} (V)	J_{SC} (mA/cm ²)	$J_{SC,sub-GaAs}$ (mA/cm ²)
1×QD-layer textured+gold	0.96	2.84	8.37×10^{-4}
1×QD-layer textured+air	0.96	2.91	1.16×10^{-3}
1×QD-layer polished+air	0.99	3.41	7.94×10^{-4}
10×QD-layer textured+gold	0.88	2.19	7.90×10^{-4}
10×QD-layer textured+air	0.88	2.35	1.21×10^{-3}
10×QD-layer polished+air	0.88	2.20	7.95×10^{-4}
Reference textured+gold	1.25	5.02	
Reference textured+air	1.26	4.88	
Reference polished+air	1.26	4.61	

not exhibit any contribution to the $J - V$ characteristic, the 1×QD-layer samples and 10×QD-layers samples exhibit sub-bandgap $J - V$ response. Briefly, these $J - V$ curves show (1) there is contribution of absorption in the QDs to the photogenerated current, and (2) in the samples, light trapping is more effective in the textured+air approach.

Table 2.2 summarizes the most representative parameters of these solar cells, where we have collected both the open circuit voltage (V_{OC}) and the short circuit current density (J_{SC}) of the solar cells.

2.5.3 Low-temperature external quantum efficiency

For measurements of the EQE at low temperatures, we used a modification of the set-up used for room temperature measurement (see Figure 2.17). The samples, already mounted on a copper disk, were placed in a closed-cycle helium cryostat. For this low-temperature characterization, the same halogen light-source was employed.

Figure 2.23 shows the EQE response of the 10×QD-layers polished+air sample as a function of the excitation photon energy measured at different temperatures. These measurements, from 300 K to 9 K, show the EQE dependence of the with the temperature. Additionally, EQE measurements of the three 10×QD-layers samples (textured+gold, textured+air, polished+air) as a function of the excitation energy at room temperature and at $T = 9$ K are shown in Figure 2.24. These figures show that, at low temperatures, while the supra-bandgap EQE is reduced approximately by one order of magnitude, the

sub-bandgap EQE is strongly reduced several orders of magnitude. This fact is due to the inhibition of thermal escape of photocarriers out of the QDs (see discussion of Figure 2.30).

Figure 2.23: *EQE* measurement of the 10×QD-layers polished+air Sample as a function of the excitation photon energy at different temperatures.

Figure 2.24: *EQE* measurement of the 10×QD-layers samples (textured+gold, textured+air, polished+air) as a function of the excitation photon energy at room temperature and cryogenic temperature (9 K).

Besides this reduction at low temperature, Figure 2.24 shows that the sub-bandgap EQE associated to the E_H transition at $T = 9$ K, which peaks around 1.47 eV, is approximately the same for all the samples. Later on, we discuss how the electrons can be collected when thermal carrier escape is inhibited (see discussion of Figure 2.30).

2.5.4 Two-photon photocurrent response

As we pointed out in Section 2.1, the QD-IB material can be employed for fabricating QD-IBSCs and OTIPs. In the previous sections we have shown the EQE response of the QD-IB devices as QD-IBSCs. In this section, we show the photocurrent response of the devices working as OTIPs. The OTIP operates in short circuit under illumination of two different photons, a supra-bandgap photon that biased the device and pumps the electrons from the VB to the CB, and a sub-bandgap (IR) photon that pumps the photons from the IB to CB, reducing the net carrier recombination via the IB. Thus, IR absorption is measured as an increase in photocurrent, what we call as *two-photon photocurrent* (TPPC).

The TPPC response of the QD-IBSCs was acquired modifying the set-up from the one employed for low-temperature EQE measurements: we employed a SiC IR lamp and a second light beam from a 560-nm LED. These PC responses were acquired at 9 K (thermal carrier escape is therefore inhibited) and illuminated by means of a monochromatic beam light obtained from a chopped IR lamp (Newport 140 W IR SiC) and directed with the aid of the monochromator. In addition, a 560-nm LED-light bias was used as supra-bandgap light source. Figures 2.25, 2.26 and 2.27 show the TPPC response for the $10\times$ QD-layers samples: textured+gold, textured+air, polished+air, respectively. The IR lamp spectrum was characterized by measuring the spectral PC in a MCT detector⁷, at 77 K, placed at the output of the monochromator. This PC response is include in the inset of the figures. In addition, the $10\times$ QD-layers devices were simultaneously illuminated by the supra-bandgap 560-nm LED, biased at three current levels (0, 20,

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⁷The Hamamatsu MCT (HgCdTe) photoconductive detector is an IR detector that exploits the photoconductive effect.

and 40 mA). The photon emission energy (2.21 eV) from the 560-nm LED is indicated in the graphs as a vertical dashed line.

Figure 2.25: Two-photon photocurrent response of the 10×QD-layers textured+air Sample as a function of the excitation photon energy from the IR lamp at $T = 9$ K illuminated simultaneously with a second light obtained from a 560-nm-LED biased at different current levels. The photocurrent response of the IR lamp measured with a MCT photodiode detector at 77 K is shown in the inset of the graph.

In these figures, we appreciate two differentiated responses: the supra-bandgap Al-GaAs response and the sub-bandgap response. The y-axis is in linear scale. While the supra-bandgap PC does not change roughly with the addition of the 560-nm LED-light bias at different current intensities, the sub-bandgap PC response (in the range 0.2–0.65 eV) increases substantially when the LED-light bias is applied, in comparison with the PC response due to IR-only illumination. The valleys measured at approximately 0.45 and 0.29 eV correspond to the atmospheric absorption of CO_2 . Results demonstrate IR two-photon response in the range 0.2–0.65 eV. We could especulate that light absorption could take place beyond 0.65 eV. However, as it can be seen in the insets, the spectrum of the IR lamp diminishes and the sample response at these energies merges with the noise level.

Figure 2.26: Two-photon photocurrent response of the 10×QD-layers textured+gold Sample as a function of the excitation photon energy from the IR lamp at $T = 9$ K illuminated simultaneously with a second light obtained from a 560-nm-LED biased at different current levels. Photocurrent response of the IR lamp measured with a MCT photodiode detector at 77 K is inset on the right side of the graph.

Figure 2.27: Two-photon photocurrent response of the 10×QD-layers polished+air Sample as a function of the excitation photon energy from the IR lamp at $T = 9$ K illuminated simultaneously with a second light obtained from a 560-nm-LED biased at different current levels. Photocurrent response of the IR lamp measured with a MCT photodiode detector at 77 K is inset on the right side of the graph.

In order to show the impact of light-trapping in the IR range, the TPPC responses of the three 10×QD-layers solar cells are depicted together in Figure 2.28. The TPPCs show the results of measurements at 9 K with the supra-bandgap LED-light biased at 40 mA. As it can be seen, the 10×QD-layer textured+air solar cell gives the highest photogenerated current in the range 0.2–0.65 eV, which is in agreement with EQE and $J - V$ measurements and experiments previously explained. To our knowledge, for the first time, light trapping via surface texturing has been demonstrated in QDs in the 0.2-0.65 eV range.

Figure 2.28: Two-photon photocurrent response of the 10×QD-layers samples as a function of the excitation photon energy at $T = 9$ K when illuminated with a second light obtained from a 560-nm-LED biased at 40 mA.

In Figure 2.29 the PC response of the 10×QD-layers textured+air device obtained when biasing the 560-nm LED-light at 40 mA is depicted altogether with the atmospheric transmittance⁸ as a function of the photon wavelength. The atmospheric transmittance shows two IR transmission windows at 3–5 μm and 8–14 μm . The first one

⁸The data have been obtained from Lord, S. D., 1992, NASA Technical Memorandum 103957, and we acknowledge Gemini Observatory for the acquisition

matches the PC response of the device. In light of this, QD-based OTIPs, and in particular, InAs/AlGaAs QD-IB devices, have potential for optical communications in applications for the 3-5 μm range.

Figure 2.29: Two-photon photocurrent response of the 10 $\times$ QD-layers textured+air solar cell superimposed to the transmittance of the atmosphere in the IR range. The photocurrent is depicted as a function of the incident photon energy of the IR beam at $T = 9$ K with the aid of the second light from a 560-nm-LED at 40 mA. The atmospheric transmittance data have been obtained from Lord, S. D., 1992, NASA Technical Memorandum 103957, and we acknowledge Gemini Observatory for their acquisition.

2.6 Impact of light trapping on InAs/AlGaAs QD-IB devices

In the previous section, all the results from the characterization measurements of the batch of nine QD-IBSC devices used in this work have been described. Although analysis and consequences from these results have been briefly advanced, in this section we are deepening in the outcomes from the experimental characterization.

The main goal of this work is to study how the self-organized texture of S-I GaAs substrate of the InAs/AlGaAs QD-IBSC prototypes enhances the photon absorption as-

sociated to the sub-bandgap transitions, E_H and E_L . For IBSC, the increment of the absorption in QDs must be achieved in both transitions. OTIPs, however, only would benefit from absorption enhancement in the E_L transition.

2.6.1 Absorption increase due to texturing

The study of the absorption improvement at the sub-bandgap range in QD-IBSCs was carried out by the self-organized texture of the undoped GaAs substrate of the samples used in this work (InAs/AlGaAs QD-IBSC structures: $1\times$ QD-layers Sample, $10\times$ QD-layers Sample and Reference Sample; see Figure 2.5).

The EQE measurements at room temperature (see Figures 2.18–2.20) as well as the low-temperature IR PC response demonstrate that the sub-bandgap photogenerated current increases when light-trapping techniques have been incorporated to the structure, as in the cases of the textured+gold and textured+air samples, in comparison with the polished+air samples. When considering the J_{SC} contribution until the n-GaAs bandgap (obtained by integrating the related ranges of the EQE) of the textured+air samples (both $1\times$ QD-layer and $10\times$ QD-layers), this is approximately a 60 % greater than the J_{SC} of the polished+air samples. This result is in agreement with the sub-bandgap $J - V$ characteristics of the QD devices (see Figure 2.22), that show an increment of the $J - V$ for the textured+air devices when a S-I GaAs wafer is placed as filter under the solar spectrum. These $J - V$ characteristics from the response of the InAs/AlGaAs QD-IBSC prototypes when considering only the contribution of photons with energies below the GaAs bandgap expose the enhancement of the sub-bandgap absorption provided by the texturing of the devices.

Moreover, the increment of the absorption as a consequence of the texturing is not observed in the supra-bandgap range. In this range, the EQE response is determined by the high-absorptivity of the AlGaAs, and, in addition, the photons not absorbed by the AlGaAs are absorbed by the GaAs substrate. Furthermore, the light-trapping effect is not seen either when measuring the total $J - V$ response (see Figure 2.21).

Despite the benefit of light trapping for photons with energies $E > E_G$, photons with energies $E_{G,Al_{0.35}Ga_{0.65}As} > E > E_{G,n-GaAs}$ are absorbed in the GaAs substrate and, thus, they are not benefited by light-trapping texturing. In future works, benefit of the light-trapping should also be applied to all photons with energies below E_G .

2.6.2 Two-photon photocurrent

The IB effect in QD-IB devices such as QD-IBSCs and OTIPs is shown by two-photon photocurrent measurements. These TPPC are conceptually different: in QD-IBSCs the TPPC is measured with two sub-bandgap photons, and in OTIPs, with one sub-bandgap photon and one supra-bandgap photon. Depending on the device, the two-photon mechanism and the IB effect can be interpreted by two ways:

- Increasing the electron-hole pair generation process through the IB that make carriers being pumped from the VB to the CB by means of the absorption of sub-bandgap photons and due to the photo-filling of the IB, which should be ideally empty.
- Decreasing the IB recombination of electron-hole pairs. The two-photon mechanism involves one supra-bandgap photon and one sub-bandgap photon. The decrease of the net recombination is achieved thanks to the absorption of sub-bandgap photons that pump electrons from IB to the CB.

In both cases (increasing the generation and reducing the recombination), the response is weak.

Figure 2.30 illustrates the IBSC/OTIP circuit model. Let us analyze the operation of the OTIP: the photogenerated current from supra-bandgap photons is represented by J_{L3} and the recombination path from the CB and VB is represented by J_{D3} (diode 3) and by currents J_{D1} and J_{D2} when the recombination occurs assisted by the IB. When IR light is added, the generation from the IB to the CB is represented by the current J_{L2} . As a consequence, the net current through the external circuit, J_{SC} , is increased by ΔJ_{SC} , when IR radiation pumps electrons from the IB to the CB. When the thermal carrier escape is

Figure 2.30: Equivalent circuit model of the QD-IBSC. It depicts the three bands, the current generators (J_{L3} between CB and VB, J_{L1} between the VB and IB, and J_{L2} between the IB to the CB) connecting the bands as carrier generation processes and the diodes carrier accounting for the recombination processes. The thermal escape process is represented as a resistance that connects the IB and the CB. This resistance allows to explain that, at room temperature, PC can be extrated when the device is illuminated with only sub-bandgap photons that pump electrons from the CB to the IB and that it almost disappears when the solar cell is cooling. However, the inverse saturation current of the diode J_{D2} explain the photogenerated current when thermal carrier escape is inhibited.

inhibited, the inverse saturation current of the diode between the CB and the IB allows the collection of the electrons when the solar cell is illuminated with photon energies $h\nu > E_H$. This ΔJ_{SC} is what we measure here as TPPC in short circuit condition and what we have described previously as a decrease of the recombination. Moving on to the operation of the IBSC, the TPPC is measured when the IBSC is illuminated with two sub-bandgap photons which will be promote an electron from the VB to the IB and an electron from the IB to the CB. This effect is what we have described above as the increament of the generation process.

The PC response in the $10\times$ QD-layers IB devices (see Figures 2.25–2.27) demonstrates, for the first time to our knowledge, that the light trapping in the textured QD-IBSC devices enhances the absorption in the sub-bandgap transition, E_L . In addition, we have measured TPPC by means of biasing the solar cells with supra-bandgap LED-light and measuring the response to the excitation energy in the IR range. This demon-

strates that the IB recombination process is reduced when the sub-bandgap photons are absorbed.

Finally, this TPPC measurement strengthens the employment of QD-IB devices as optoelectronic IR detectors since the net recombination is reduced in the $10\times$ QD-layers optically triggered infrared photodetectors, with no-voltage bias needed, as well as it reinforces the light-trapping effect in QD-IBSC for sub-bandgap photons.

2.7 Conclusions

In this Chapter, we have studied the impact of light-trapping techniques applied to QD-IB devices, with the aim of increasing the absorption of photons in the QDs. We have obtained the following conclusions:

- Surface texturing (via $\text{NH}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$) is an effective means of implement light trapping at sub-bandgaps transition energies in QD-IB devices. Using this approach we have demonstrated absorption enhancement in InAs/AlGaAs QDs. In particular, we have demonstrated for the first time light trapping via surface texturing in QDs in the 0.2-0.65 eV range.
- The best results have been obtained by combining the self-organized texturing of the S-I GaAs substrate of the InAs/AlGaAs QD-IBSC with air, instead of a back gold reflector. From the $J - V$ characteristics, the $J_{\text{SC,sub-GaAs}}$ values of the $1\times$ QD-layer textured+air Sample is 46 % greater than the corresponding values of the non-textured cases one. For the case of $10\times$ QD-layer textured+air Sample the relative increment is around 52 % greater than for the non-textured case. When the textured+gold samples are considered, the relative increment is negligible.
- The implementation of surface texturing to InAs/AlGaAs OTIPs improves their response to the IR. The spectral response of the devices (3-5 μm) supports the use of QD-based OTIPs in optical communications through the atmosphere.

Chapter 3

Demonstration of two-photon photovoltage in QD-IBSC

3.1 Introduction

As it was described in the first chapters, the IB allows electron interaction with sub-bandgap energy photons ($\varepsilon < E_G$) by means of carrier generation and recombination processes. We have already explained that one of the key operational principles of the IBSC is the two-photon sub-bandgap photocurrent, through the generation of electron-hole pairs—with one electron in the CB and one hole in the VB—by means of the sequential absorption of two photons of different energy both with lower energy than the bandgap E_G . Besides, the different kinds of two-photon processes have been interpreted, on one side, as an increase in the electron-hole pair generation rate and, on the other side, as a reduction in the electron-hole pair recombination. The exploitation of the first process is one of the keys for increasing the conversion efficiency of IBSC. While, the exploitation of the second process opened up a new line of research of OTIP, which has been briefly explained in Chapter 2.

The technology investigated up to this moment in this Thesis to implement the IB is based on InAs/AlGaAs QD devices in which both two-step, two-photon processes have already been demonstrated [Ram 14b, Tam 15, Ram 14c]. The IB of this QD system is

formed by confined electronic states in the conduction band of the QD material. This means that the confined carriers that populate the IB are electrons. For this reason, we will say that this family of optoelectronic devices is *electron based*. However, recent results also point to *hole-based* quantum-dot systems as good candidates for IB materials. In particular, the two processes have been recently demonstrated in GaSb/GaAs QD samples [Wag 14, Ram 17]. In *hole-based* devices, the IB is formed by confined electronic states in the valence band of the QD material.

3.1.1 Aim of this Chapter

The first pillar of the high conversion efficiency potential of IBSCs is two-photon sub-bandgap photocurrent. It was presented in Chapter 1 and studied in Chapter 2. The second pillar is voltage preservation. This states that the extra recombination introduced by the IB does not limit the output voltage of the devices [Luq 97]. In other words, albeit below-bandgap photons participate in the generation of photocurrent, the output voltage of the device can exceed the absorption threshold energy (divided by the electron charge) and is only limited by the bandgap E_G . This is so because, since the generation of electron-hole (CB-VB) pairs via the IB is a series-connected process, the chemical potential of subsequently absorbed photons adds up to the total electro-chemical potential of the photo-generated electron-hole pair. Voltage preservation has been proven in electron-based IBSCs under supra-bandgap illumination [Ant 10b, Lin 12].

Yet, the direct demonstration of the effective contribution of two-photon absorption to the preservation of the output voltage remained elusive. This is that we call *two-photon photovoltage* (TPPV). In this work, we study for the first time the impact of two sub-bandgap photons on the open-circuit voltage (V_{OC}). The TPPV is defined then as the increase of the open-circuit voltage (V_{OC}) of a solar cell due to two-photon sub-bandgap absorption.

The TPPV in IBSC can be explained by the occurrence of two-photon, two-step absorption processes, whereby an electron is excited from the VB to the IB and this, or another, from the IB to the CB in two different two-particle-collision processes. We

should remember that the output voltage of a solar cell, V , and thus the V_{OC} , is just equal to μ_{CV} divided by e and that V is only limited by E_G (see Figure 1.2). When considering the IB, this involves the existence of the third QFL, ε_{FI} —accordingly with what was presented in Figure 1.1 and we show again in Figure 3.1— and the consequent QFL splits, $\varepsilon_{FI} - \varepsilon_{FV}$ and $\varepsilon_{FC} - \varepsilon_{FI}$. These QFL splits do not limit the V_{OC} since $\mu_{CV} = (\varepsilon_{FC} - \varepsilon_{FI}) + (\varepsilon_{FI} - \varepsilon_{FV})$ is fulfilled.

Figure 3.1: Simplified band diagram of an IB material.

To study this TPPV type-II GaSb/GaAs QD-IB devices have been fabricated at the University of Michigan. We have adapted the set-up for measuring TPPC, previously described, to carry out the measurements.

In Section 3.2 we present the QD-IBSC prototypes used in this work. After that, in Section 3.3 we describe the TPPC and the TPPV results. The TPPC results will help us to analyse and understand the TPPV results, which we will do in Section 3.4. Finally, we will summarize the main outcomes of this work in Section 3.5.

This work was carried out in collaboration with the Department of Electrical Engineering and Computer Science, University of Michigan, in USA, with the Group of Prof. J. Phillips.

3.2 Description of the GaSb/GaAs QD-IBSC

GaSb/GaAs QDs exhibit a type-II (staggered) band lineup with confinement of holes only [Wal 89, Hat 95, Suz 99] as depicted in Figure 3.2. In this material, the CB and the VB correspond to those of the host material (GaAs) and the IB is formed by the confined hole states introduced by the QD material (GaSb). For simplicity, only the deepest confined hole state—the ground state—has been represented in Figure 3.2. Note that in this material the IB is closer to the VB than to the CB, and the sub-bandgaps E_H and E_L are denoted accordingly.

Figure 3.2: Type-II band lineup of GaSb/GaAs QDs. The confined state of the QD is shown as the IB. The two sub-bandgaps induced by the IB, E_H and E_L , are indicated as well as the bandgap of the GaAs host, E_G .

IB devices with an IBSC structure including 10 layers of GaSb/GaAs QDs were fabricated by the University of Michigan. Their semiconductor layer structure is sketched in Figure 3.3. The GaSb/GaAs QD diode structures were grown by MBE on heavily n-doped GaAs (100) substrates. Samples consist of a GaAs p-n junction with the QD-stack in the n-side near the junction. GaSb QDs were grown via the S-K growth mode with 2.3ML nominal thickness of a GaSb layer on an Sb-terminated (2×8) surface reconstruction. All QD layers were immediately capped by a 30 nm GaAs layer. AlGaAs window and back-surface-field layers were grown on top of and below the p-GaAs and the n-GaAs emitters, respectively, in order to minimize carrier recombination at the interfaces with the metallic contacts. The full layer structure of the diode is shown in Figure 3.4.

Figure 3.3: Fabricated GaSb/GaAs IB samples. The semiconductor layer structure of the fabricated samples is depicted in (a). The QD stack consists of 10 layers of GaSb QDs. Images (b) and (c) show HRTEM micrographs. In particular, image (b) shows three consecutive QD layers and (c) a magnification of one QD layer. Zones rich in Sb appear darker in the images than zones rich in As. The big yellow arrows in (c) point at the GaSb QDs. The small red arrows delimit the width of the GaSb wetting layer. A dotted white line, encircling a trapezoid, depicts the cross section of one QD.

Device structures were fabricated using standard photolithography, metallization, and etching techniques. The MBE growth GaAs p-n junctions were processed into square solar cells of area 6.84 mm^2 . All devices were mesa isolated, with ohmic metal contacts provided by Pd/Zn/Pd/Au and Ni/Ge/Au/Ti/Au for p-type and n-type GaAs, respectively, followed by rapid thermal annealing at 400°C . An anti-reflection coating of ZnS and MgF_2 was deposited on the top surface.

Figure 3.3 (b) and Figure 3.3 (c) show cross-sectional high-resolution transmission electron microscopy (HRTEM) images of the QD stack of one of the samples. Figure 3.3 (b) shows the first three layers (from bottom to top in the structure) of GaSb QDs. A

contact	200nm p+GaAs (2e19)
window	30nm p+ Al _{0.2} Ga _{0.8} As (2e18)
p emitter	500nm p+GaAs (4e18)
n emitter	150nm n+GaAs (1e16)
QD stack	10 layers of n+ GaSb dots (~220-330nm total) doping is graded from (1e17 to 1e16) GaAs 1e16 QD's + GaAs 1e16 GaAs 1e16 QD's + GaAs 1e16 GaAs 1e16 QD's + GaAs 1e16 GaAs 1e16 QD's + GaAs 1e16 GaAs 2e16 QD's + GaAs 2e16 GaAs 3e16 QD's + GaAs 3e16 GaAs 4e16 QD's + GaAs 4e16 GaAs 5e16 QD's + GaAs 5e16 GaAs 6e16 QD's + GaAs 7e16 GaAs 8e16 QD's + GaAs 9e16 GaAs 1e17 GaAs 1e17
n emitter	2500nm n+ GaAs (1e17)
back surface field	150nm n+ Al _{0.3} Ga _{0.7} As (1e18)
substrate	300nm n+GaAs (2e18)

Figure 3.4: Layer structure of the studied GaSb/GaAs QD devices.

high density of closely spaced QDs is deduced from the image, with an inhomogeneous size distribution. Most QDs have a lateral size smaller or equal to 10 nm, while the QD height is in the range of 3–4 nm. A single QD layer is shown in Figure 3.3 (c), where the yellow arrows point at the GaSb QDs, while the red arrows indicate the width of the GaSb wetting layer (approximately 1 nm), a defining characteristic of the Stranski-Krastanov growth mode. Further details of the structural properties of GaSb/GaAs QDs growth under these conditions are described in [Mar 13].

3.3 Two-photon measurements

After we have described the samples used for this work, this section is devoted to show the two-photon measurements carried out, that is, the two-photon photocurrent (TPPC) and the two-photon photovoltage (TPPV).

For the TPPC measurements, the set-up employed was described in Section 2.5. Two light sources (henceforth “photon1” and “photon2”) could illuminate simultaneously

the sample. Photon1 (a SiC lamp) was chopped and directed into a three-grating 1/4 m monochromator. Photon2 (which could be turned on or off) was a 1.32-eV laser diode.

The experimental set-up used for these TPPV measurements is a modification of the TPPC set-up previously described in Section 2.5, so that the ΔV_{OC} of the solar cells, instead of the current (ΔJ_{SC}), is now measured. Again, two light sources could illuminate simultaneously the samples. And in this case, samples were connected to a voltage amplifier. The final signal detection was made using a lock-in amplifier to measure at the chopping frequency (6 Hz).

3.3.1 Two-photon photocurrent (TPPC)

Before analyzing the results, we would like to highlight the fact that we have used a SiC IR lamp as source for photon1. Photocurrent response of the IR lamp measured with a MCT photodiode detector at 77 K is shown in Figure 3.5. The blackbody emission of the source peaks at around 0.4 eV and decays rapidly for higher energies. This will be important to understand quantitatively the results.

In Figure 3.6, we show the spectrally resolved TPPC of the GaSb/GaAs QDs and its dependence with the increment of the intensity of photon-fluxes. The energy of photons named “photon1”, E_{ph1} , can be tuned between 0.2 and 1.9 eV. The energy of photons named “photon2”, E_{ph2} , is kept constant at 1.32 eV, which, as we shall see, fulfills the condition $E_H < E_{ph2} < E_G$. In these measurements, signal response to photon1 is monitored via lock-in techniques, while photon2 sets the steady-state conditions of the measurement. Samples are measured under short-circuit conditions; i.e., no electrical power is supplied to the device under test. The magnitude measured is $\Delta J_{SC} = J_{SC} - J_{SC,ss}$, where $J_{SC,ss}$ is the steady-state photogenerated current under photon2 illumination and J_{SC} is the total response under the addition of photon1.

Figure 3.6 shows the results of the TPPC measurements at $T = 9$ K. The y-axis represents the photogenerated current (ΔJ_{SC}) of the IBSC prototypes in response to photon1 illumination, whose energy is represented on the x-axis. The black line corresponds to the case of photon1-only illumination, $\Delta J_{SC,1ph}$. Three energy absorption

Figure 3.5: Photocurrent response to the IR lamp measured of a MCT photodiode detector at 77 K. It is plotted against the same energy range than the TPPC and TPPV for later discussions.

Figure 3.6: Two-photon photocurrent measurements at $T_{\text{cryostat}} = 9$ K. The three absorption bandgaps, E_G , E_H , and E_L are indicated. The black line corresponds to the case in which only photon 1 is used to illuminate the cell: $\Delta J_{\text{SC},1\text{ph}}$. The coloured ΔJ_{SC} lines correspond to the two-photon illumination case, $\Delta J_{\text{SC},2\text{ph}}$, for different intensities of photon2, $E_{\text{ph2}} = 1.32$ eV.

thresholds can be identified, corresponding to E_G , E_H , and E_L , indicated by the dashed lines in Figure 3.6. $E_G = 1.52$ eV corresponds to the GaAs bandgap at 9 K. E_H , as defined in Figure 3.2, is related to the transition of the ground state for holes in the QDs to the bottom of the CB. $\Delta J_{SC,1ph}$ shows a smooth signature in the 1–1.1 eV range. E_H is within the range of prior reports (1.0–1.3 eV) [Hat 95, Suz 99, Hat 98, Sun 96, Alo 07], though closer to the lower limit. Sb-As interchange and the shape of the dots may explain the variations of E_H [Now 12]. The value of E_L –the confining energy identified with the IB– is 0.49 ± 0.01 eV. This value was obtained in [Ram 17] from photocurrent measurements on the same devices. In the samples E_L is somewhat higher than previous values reported in the literature [Wag 14, Gel 03], with the exception of the value reported in [Now 12]. The high value of E_L is in agreement with the low value of E_H since both have to add up to E_G . Note that, in the QDs, $E_H + E_L \approx 1.51 \pm 0.01$ eV $\approx E_G$, as expected for type-II QDs.

Under photon1-only illumination, the response for $E_H < E_{ph1} < E_G$ shows how the signal $\Delta J_{SC,1ph}$ peaks at around 8×10^{-10} mA·cm $^{-2}$ and, in particular, $\Delta J_{SC,1ph}(E_H) \approx 2 \times 10^{-10}$ mA·cm $^{-2}$. For $E_{ph1} < E_H$, $\Delta J_{SC,1ph}$ diminishes until it merges with the noise level of the measurement for $E_{ph1} < E_L$. The low value of the sub-bandgap $\Delta J_{SC,1ph}$ is explained by the lack of an efficient mechanism –under monochromatic sub-bandgap illumination– to complete the remaining second optical transition that would enable photocurrent.

Let us now analyse the impact that the variation of the intensity of the illumination associated to photon2 has in the different energy ranges of the TPPC results (coloured lines in Figure 3.6, $\Delta J_{SC,2ph}$). For all the intensities, the TPPC greatly increases with the addition of photon2 in the energy range near E_L . This result indicates that the two-photon process takes place in the hole-based IBSC. When photons2 are absorbed, holes are created in the IB, enabling the absorption of photons and, therefore, the generation of photocurrent. Under different photon2 intensities, $\Delta J_{SC,2ph}$ remains constant or slightly reduces for $E_H < E_{ph1} < E_G$. At these energies, the measured $\Delta J_{SC,2ph}$ is in the same range than $\Delta J_{SC,1ph}$. Finally, for $E > E_G$ the TPPC results change only slightly, with no clear dependence with the intensity of photon2.

3.3.2 Two-photon photovoltage (TPPV)

Figure 3.7: Two-photon photovoltage measurements at $T_{\text{cryostat}} = 9$ K. The three absorption bandgaps, E_G , E_H and E_L are indicated with dashed lines. $E_{\text{ph2}} = 1.32$ eV is also indicated. The black line corresponds to the case in which only photon 1 is used to illuminate the cell: $\Delta V_{\text{OC},1\text{ph}}$. The coloured lines correspond to the two-photon illumination case, $\Delta V_{\text{OC},2\text{ph}}$, for different intensities of photon2. The inset is a magnification of the $E_L < E < E_H$ range of the measurement.

Using our two-photon set-up we have performed the first two-photon photovoltage measurements in GaSb/GaAs QD samples. The results at 9 K are shown in Figure 3.7. The sample is illuminated with two monochromatic light beams, just as in the case of the TPPC results of Figure 3.6. $E_{\text{ph2}} = 1.32$ eV while E_{ph1} is swept from 0.2 to 1.9 eV. The intensity of photon2 is constant during one sweep but changed for the next one¹. The y-axis plots the measured increase in open-circuit voltage, V_{OC} , when both light beams are illuminating the sample. It is important to remark that, because the measure-

¹The intensities of photon2 in these TPPV measurement are not equal to the ones in the TPPC measurement. The response of each experiment is different each other. Moreover, the measurement conditions changed because the experiments were carried out in different days. In addition, the response of the 1.32-eV laser diode with the intensity could change.

ment is locked to photon1 excitation, the measured photovoltage is the variation in V_{OC} , $\Delta V_{OC,2ph}$, due to the addition of photon1 with respect to the steady-state V_{OC} , $V_{OC,ss}$, value induced by the continuous-wave photon2 illumination.

The black line represents the measurement when photon2 is OFF; i. e., when photon1-only illumination is used ($\Delta V_{OC,1ph}$). Note that, in this case, $\Delta V_{OC,1ph}$ equals the total V_{OC} , because $V_{OC,ss} = 0$. Let us analyze for this case the three energy ranges of interest. For $E > E_H$, V_{OC} is greater than zero, peaking at around 1.5 mV. For $E_H < E < E_G$, ΔV_{OC} is in the 0.5–0.8 mV range. The abrupt fall in $\Delta V_{OC,1ph}$ for energies just below E_G is due to the strong reduction in absorptivity (and hence in photo-generated carriers) in the GaSb QDs as compared to the GaAs bulk (as it is shown in the TPPC results of Figure 3.6). $\Delta V_{OC,1ph}$ increases again for lower energy values following the recovery in the photon flux intensity. Below 1.1 eV, $\Delta V_{OC,1ph}$ decays rapidly again, following the decrease in $\Delta J_{SC,1ph}$, and finally goes to zero for $E < E_H$. In summary, as expected, the spectral $\Delta V_{OC,1ph}$ is consistent with $\Delta J_{SC,1ph}$. The measured photocurrents are in the sub nA range (see Figure 3.6), which in turn explain that the measured $\Delta V_{OC,1ph}$ values are in the mV range.

With the addition of photon2, finite two-photon ΔV_{OC} ($\Delta V_{OC,2ph}$) is measured for $E > E_H$, where V_{OC} is greater than zero, peaking at around 1.5 mV. For $E_L < E < E_H$, ΔV_{OC} increases with the intensity of photon2 (see inset of Figure 3.7). These results demonstrate, for the first time, an increase in V_{OC} of GaSb/GaAs QD intermediate band solar cells resulting from two-photon sub-bandgap illumination. We call this phenomenon two-photon photovoltage (TPPV). Furthermore, our measurements spectrally resolve which photon energies contribute more efficiently to this phenomenon. For $E > E_H$, ΔV_{OC} decreases with increasing photon2 intensity.

3.4 Analysis of the two-photon measurements

In this section, we will assess how TPPC and TPPV are correlated. The TPPC and TPPV results under two-photon illumination show that two-photon sub-bandgap process takes place in the hole-based GaSb/GaAs IBSCs.

The decrease in $\Delta V_{OC,2ph}$ for $E_H < E < E_G$ is consistent with the sub-bandgap response of the GaSb/GaAs devices. On the contrary, the decrease in $\Delta V_{OC,2ph}$ for $E > E_G$ does not seem to correlate, at first sight, to $\Delta J_{SC,2ph}$, where $\Delta J_{SC,2ph}$ is shown not to have an apparent dependence on photon2. In reality, the $\Delta V_{OC,2ph}$ and $\Delta J_{SC,2ph}$ results are indeed consistent, as we explain next. Our results show in fact $\Delta V_{OC,2ph} = V_{OC,2ph} - V_{OC,ss}$, where $V_{OC,2ph}$ is the total open-circuit voltage under two-photon illumination.

It is straightforward to derive from Shockley's diode equation that

$$\Delta V_{OC,2ph} \sim \ln \left(\frac{I_{L,2ph}}{I_{L,ss}} \right) \quad (3.1)$$

where $I_{L,2ph}$ and $I_{L,ss}$ are the photo-generated currents under two-photon illumination and steady-state-only (photon2) illumination, respectively. If we define

$$\Delta I_{OC,2ph} = I_{OC,2ph} - I_{OC,ss} \quad (3.2)$$

then

$$\Delta V_{OC,2ph} \sim \ln \left[1 + \left(\frac{\Delta I}{I_{L,ss}} \right) \right] \quad (3.3)$$

From Equation 3.3, for constant ΔI , $\Delta V_{OC,2ph}$ will decrease if $I_{L,ss}$ increases. Going back to our results, Figure 3.6 shows that, for $E > E_G$, $\Delta J_{SC,2ph}$ is roughly constant with photon2 illumination. In the case of Equation 3.3 this will imply constant ΔI . However, an increase in photon2 implies an increase in the steady-state current flowing through the devices. In the case of Equation 3.3 this implies an increase in $I_{L,ss}$. Therefore, it is expected that $\Delta V_{OC,2ph}$ will be reduced with increasing intensity of photon2, even if $\Delta J_{SC,2ph}$ remains constant. In fact, the increase in $V_{OC,ss}$ as $I_{L,ss}$ increases should also affect the measured $\Delta V_{OC,2ph}$ for $E > E_G$, which means that part of the ΔV_{OC} decrease in the $E_H < E < E_G$ range is not due to the reduction in ΔI but to the increase in $I_{L,ss}$ following photon2 intensity.

Finally, we want to point out that the E_L peak is located at different energies in both two-photon measurements, TPPC (see Figure 3.6) and TPPV (see Figure 3.7). From

what we just said, TPPV and TPPC phenomenons are correlated, showing an apparent anti-symmetrical performance, except for the range $\varepsilon < E_L$. It seems that, even if absorption at E_L is efficient in the production of TPPC, it is not efficient in the production of TPPV. The reasons for this are at this moment unclear.

3.5 Conclusions

In this Chapter, we have studied two-photon measurements in GaSb/GaAs QD-IBSCs. From this work we can establish the following summary and conclusions:

- In GaSb/GaAs QD-IBSCs, the addition of a second beam of photons with energy $E_H < \varepsilon < E_L$ produces an increase in V_{OC} with respect to illumination only with photons of energy $E_G < \varepsilon < E_H$. This two-photon photovoltage phenomenon represents a key demonstration in IBSCs which had been elusive until now.
- We have correlated theoretically the generation of TPPV and the production of TPPC. We have verified qualitatively and empirically this correlation. Theoretically, the production of TPPC should be accompanied by the generation of the TPPV. In the experiments one photon had constant energy $h\nu > E_H$ and the other variable energy $h\nu \geq E_L$. Surprisingly, when the energy of the latter photon was E_L , the production of TPPC is not accompanied by the generation of TPPV. This result is still under study.

Chapter 4

Development of a substrate removal processing method for III-V solar cells compatible with low-temperature characterization

4.1 Introduction

As introduced in Chapter 2, light-trapping techniques could be applied with thin-film solar cells¹. As anticipated in Chapter 1, there has been interest in solar cell research and industry in reducing the thickness of conventional thick –a few hundred microns– devices [May 15, Ham 13, Gre 07]. The reasons that make thin-film solar cells attractive are diverse. For solar cells made of direct-gap semiconductors, which need only a few microns to absorb most of the sunlight, manufacturing cost could be reduced by reutilizing several times the substrate on which the solar cells structures are grown, following the so-called epitaxial lift-off (ELO) process [Yab 87]. Without the thick substrate, the thin-film structures can be transferred onto a flat or curved support, e.g.,

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¹In this context, a thin-film solar cell refers to a device with a thickness that varies from a few microns to a few tens of microns, depending on the absorbing material.

glass [Van 97], quartz substrate, silicon [Gei 07], plastic foil [Sch 06, Pag 08] or metal foil [Tak 06]. This makes it possible to incorporate solar cells in flexible electronics designs [Sch 06, Sun 07, Pag 08]. Furthermore, removing the substrate is required in inverted solar cells, conceived to increase the flexibility in the design of layers structure of multijunction solar cells [Yu 13, Gei 08]. Finally, being of interest to us, the combination of a thin-film structure with light trapping techniques, which effectively increase the optical length of the devices, may lead to physically thin but optically thick (highly absorbent) solar cells [Mar 97]. Related to this, thin-film device processing has caught the attention of researches working on solar cells based on nanostructures, such as inorganic quantum dot [Ben 13, Sog 14] or quantum well [Wat 14, Wat 15, Ino 15] solar cells. In those works, surface texturing [Yab 82] of thin-film devices is explored as a means of enhancing low-energy-photon absorption in the nanostructures.

Low-temperature characterization in novel solar cell concepts, such as QD-IBSC, as well as in other devices exploiting quantum structures [Pet 82, Cib 86, Fel 87, Lev 93, Mar 08b, Ram 14c], has already proven to be essential in order to understand the fundamental principles, potential and limitations of solar cells using inorganic nanostructures [Elb 12, Yos 14, Ram 14d]. In particular, low-temperature characterization is needed for preventing thermal carrier escape in QD-IBSCs. The importance of the low-temperature characterization of solar cells has been shown in the results of Chapter 2.

Additionally, as previously mentioned in Chapter 1, one hot topic in QD-IBSCs is to enhance the absorptivity of the quantum structures by using light trapping mechanisms in thin-film devices. The work carried out so far has proven the beneficial aspects of light trapping schemes [Sog 14, Ben 13, Wat 14, Wat 15, Ino 15]. However, the experimental results obtained are limited to room temperature conditions, since the thin-film processing methods used are not compatible with low-temperature measurements. The reason is that thin-film solar cells are usually manufactured through the bonding of the solar cell structure and the support with a polymeric epoxy, which is not a good electrical or thermal conductor [Van 97, Sch 06, Gei 07, Pag 08, Gei 08]. This prevents heat dissipation as well as extracting the back contact directly from the rear side of the solar cell. Although some methods have successfully addressed the issue of heat dissipa-

tion [Tse 09, Wan 14], low-temperature characterization has not been performed on the processed devices. Only recently, low temperature measurements have been carried out in a thin-film (50 microns) device soldered with a conductive epoxy on elastomeric substrates [Lee 16]. In the latter work, measurement results at temperatures lower than 150 K are reported to be abnormal.

In this chapter, we report on a substrate removal processing method for III-V solar cells compatible with very low temperature characterization (20 K) and very thin (1.74 μm) devices. The key element of our method is the use of indium for bonding the few-micron-thick structure to a silicon flat support. Both indium and silicon are sufficiently good thermal conductors, whose thermal conductivities are approximately $82 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $148 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively [Lid 09]. Using this method we have fabricated and characterized thin-film AlGaAs solar cells² with and without a layer of InAs quantum dots (QD). Recently, the transfer onto an external substrate of a thin-film GaN light-emitting diode by using an In sheet has been reported [Kob 12]. In that work, only room-temperature operation is reported. We demonstrate our method to be suitable for low-temperature measurements because it allows for heat dissipation through the rear bonding and does not produce thermal-stress-induced mechanical strain in the thin devices. This is demonstrated by opto-electrical characterization of the fabricated solar cells at different temperatures in the 20-300 K range. Additionally, we are able to demonstrate sub-bandgap PC and thermal carrier escape in thin-film QD solar cells. Finally, the indium soldering allows electrically back contacting the device, in contrast to other thin-film processing methods [Yon 94, Gei 08, Lee 12, Lee 16], in which both the positive and negative contacts must be fabricated on the front side of the device.

It is important to highlight that here we find a meeting point between the low-temperature characterization and light-trapping techniques, which is of interest to us: the first step to apply, in the future, advanced surface texturing techniques on thin-film devices is the processing method presented here. For applying texturing techniques on surfaces we would need first further development of the thin-film devices, such as the solar cells presented in this Chapter, which has been carried out for the first time in our

²In this Chapter thin-film solar cells are referred to those based on semiconductor epitaxial growth.

group. The fabricated devices would take the advantage at least of providing a two-fold increase in the optical length of the absorbing layers due to the light reflection on the rear metal used for bonding the structure at the same time it allows us to measure the devices at low-temperature.

The work presented in this chapter has been carried out in collaboration with the group of Dr. J. M. Ripalda at IMM that has grown the layer structure of the solar cells by MBE.

4.2 Developing our processing method

In this section we describe the procedure of our processing method, from the growth of the samples to the attainment of complete devices.

4.2.1 Sample description

The samples used in this work were grown by MBE at the IMM. They consist of AlGaAs p-i-n epitaxial solar-cell structures on GaAs wafers (depicted in Figure 4.1 (the drawing is not to scale)). We call the samples S1 and S2. Both solar cells have the same structure, except for a layer of InAs QDs which is present in S2 and not in S1. It consists of an inverted structure since, at the end, the upper part of the grown structure (p type) will be the bottom part of the completed device, and the bottom part of the structure (n type) will become the upper part of the device. The device structure was grown by MBE on a 2" n-type (001) GaAs wafer. Following a 300 nm buffer layer of GaAs, a 100 nm layer of AlAs was grown to serve as SEL³ for the previously discussed substrate removal process. Henceforth, we will refer to this layer as SEL-1.

The structure is designed as to withstand n-contact annealing. For this reason, SEL-1 is followed by a 300 nm thick n-type ($3 \times 10^{18} \text{ cm}^{-3}$) GaAs contact layer. A thick layer is necessary to stop gold from diffusing into the active part of the device during contact annealing. To avoid parasitic absorption of the contact layer –which does not

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³The purpose of a stop etching layer is to act as a barrier to stop selectively a chemical etching.

Figure 4.1: Sketch of the inverted semiconductor layer structure of the thin-film AlGaAs solar cells. Sample S2 is depicted here. Both samples, S1 and S2, share the same epitaxial structure, except for the InAs QD layer which is present in sample S2.

contribute to PC generation—, it has to be selectively etched, using the metal grid as a mask. In order to prevent subsequent layers to be etched, a 5-nm AlAs SEL—henceforth SEL-2—is necessary to protect the rest of the epitaxy. Immediately after contact-layer removal, SEL-2 itself is etched in diluted HF. Below SEL-2, a 5-nm GaAs layer is left as protection against oxidation in air of the window layer. The window layer has a 78 % aluminum content and is 30-nm thick. The emitter is 200-nm thick and doped to $5 \times 10^{17} \text{ cm}^{-3}$ with 35 % Al. Thicker emitters were found to compromise the EQE at short wavelengths, probably due to a poor hole diffusion length. A 600-nm-thick AlGaAs intrinsic layer was grown between the emitter and the base. Embedded in this layer, one layer of InAs QDs was grown in sample S2. The QDs were self-assembled after the deposition of 2 monolayers of InAs. Slab doping with silicon was employed so as to dope the dots with approximately one electron per dot, assuming a QD areal density of $3 \times 10^{10} \text{ cm}^{-2}$. A 200-nm-thick Be-doped base was then grown, followed by 200 nm p+ back surface field (BSF) layer with 41 % Al to confine minority electrons away from the back side contact. The last epitaxial layer was a 100 nm thick p++ doped (from $7 \times 10^{18} \text{ cm}^{-3}$ to $3 \times 10^{19} \text{ cm}^{-3}$) GaAs layer that served as back selective contact. The total thickness of the active epitaxial layers is 1.74 μm . This will also be the thickness of the final device, excluding the metal contacts.

4.2.2 Description of the processing method

Our thin-film solar cell processing method consists in soldering with indium foil an inverted solar cell structure onto a flat silicon support. Here we have used a silicon wafer as flat support for convenience, but other flat supports could be used instead of it. Indium is the key element of the method, since it allows both heat dissipation and rear-contacting the device. Indium was employed because of its suitable features, namely, low tensile strength [Ree 88], and high thermal and electrical conductivity. The low value of indium tensile strength allows low-temperature measurements without strain-induced degradation of the sample. In addition, thermal and electrical conduction allow, respectively, for heat dissipation and back contacting of the devices. The use of indium

foils was required in order to maintain the devices flatness after soldering and removal of the substrate. The use of manually spread melted indium, which we had previously tested, resulted in a wrinkled surface and damaged devices.

As flat support we use a p-doped silicon wafer, but other thermally conductive rigid supports can be envisaged. Silicon was chosen since it is a good thermal conductor ($150\text{--}300 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). The solar-cell epitaxy needs an inverted design since it will be soldered upside-down onto the silicon support to then remove the substrate.

After soldering the structure to the support, the semiconductor substrate is removed and the final device is fabricated on the active epitaxial layers by means of standard photolithography techniques and contact fabrication using electroplating techniques.

Finally, external connection is made by wiring the thin-film solar cells. These wires are directly connected to both the front and back sides of the solar cells, so it is not necessary to fabricate both contacts from the front side of the solar cell as in the devices in Chapter 2, thus simplifying the process of contact fabrication.

Below, we describe the main steps of the developed method, illustrated in Figure 4.2, which is not to scale, applied to the AlGaAs samples.

a) *As-grown sample*

The process of fabrication begins with the samples growth by MBE. In Figure 4.2 (a) the epitaxial layers are depicted together as a single orange layer atop the n-type GaAs substrate (in blue).

b) *Front side (back contact) metallization of solar cell and Si wafer*

The first step of the processing method itself is the front side metallization of the solar cell and the Si wafer. The upper surface (which corresponds to the epitaxial growth) of the AlGaAs solar cell and the Si wafer were coated with Cr/Au (50 nm/500 nm) by thermal evaporation⁴. The Cr/Au is depicted in Figure 4.2 (b) as a golden layer atop the solar cell and the Si wafer. Cr/Au can form an ohmic contact to p-type GaAs. This Cr/Au metallic layer will be the back contact of the

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⁴The thermal operation was done making use of the Multi-technique coating system PVD-MT/2M3T manufactured by VAKSIS

solar cell and will operate at the same time as back reflector, providing ideally a two-fold increase in the optical length of the absorbing layers.

c) *Soldering in vacuum*

The solar cell and Si wafer were placed on a hotplate inside a vacuum chamber with the indium foil (50 μm) in between the two Au surfaces, as it is represented in Figure 4.2 (c). The vacuum chamber prevented the formation of air bubbles in between the metal surfaces during soldering. Additionally, an external weight was placed manually onto the wafer stack to add pressure and achieve a homogenous and flat soldering.

The hotplate was heated up to a temperature, T_{hotplate} , of 195°C and bonding occurred above 160°C, when indium melted, $T_{\text{IndiumMelting}}$, and alloyed with Au. The hotplate is maintained at 195°C for 5-10 minutes for extracting the air bubbles from the sandwich. The colling is carried out in vacuum until $T_{\text{hotplate}} < T_{\text{IndiumMelting}}$. The last part of the colling is carried through in N_2 atmosphere.

Finally, the bonded stack is removed from the hotplate when the chamber is at atmosphere pressure and the temperature is $T_{\text{hotplate}} \approx 40\text{-}50^\circ\text{C}$.

d) *Substrate removal*

The GaAs substrate of the samples was removed using a two-step etching process: (I) a quick non-selective etch with $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ (1:1), which etched away the majority of the GaAs substrate at a rate of 5-10 $\mu\text{m}/\text{min}$, and (II) a slow, selective etch the citric acid: H_2O_2 (5:1), which etched the remaining GaAs substrate until reaching the AlAs stop etching layer. SEL-1 was subsequently removed by wet etching in $\text{HF}:\text{H}_2\text{O}$ (1:10) to avoid oxidation of the surface of the AlAs SEL-1. Thus, the epitaxial n-GaAs contact layer surface became the new front side of the thin-film solar cell, where the top contacts would be next placed.

In the sketch of Figure 4.2 (d) it is seen how the thin-film solar cell is now bonded to the Si wafer with the indium foil.

e) *Photolithography*

Standard photolithography techniques were used for creating photoresist patterns on the sample. For this photolithography we have used negative photoresist deposited making use of a spin coater and cured with an UV-light lamp in a mask aligner. The simplified scheme of this process is depicted in Figure 4.2 (e).

f) *Front contact metallization of the solar cell*

The metal grid as top contact was made by Au electroplating. For the first time in our group, we incorporated electroplating techniques for depositing the metal grid of solar cells. Some pictures from the set-up are displayed later on in the next section. The thickness of the grid was in the range of 1–3 microns, represented in Figure 4.2 (f), which was characterized with a profilometer.

g) *Completion of the devices*

Lift-off of the photoresist after metallization, n-GaAs contact-layer etching, SEL-2 removal, and mesa etching completed the process to isolate each solar cell (1-mm radius). For this, standard processing techniques were used.

h) *External electrical connection*

Thin gold wires (25- μm diameter) connected the front metal grid of the devices to an external printed circuit board (PCB), as depicted in Figure 4.2 (h). The thin Au wires were bonded to the front grid with a silver conductive epoxy. Wedge wire-bonding could not be applied since it strongly damaged the thin (1.74 μm) devices. Consequently, the bonding of the thin gold wires on the grid contact had to be manually done. This step was critical because manual connection can shortcircuit the devices if the silver conductive epoxy is placed into the mesa trench. For external connection, thicker copper external wires were soldered with tin to the PCB.

Figure 4.2: Sketch of the key steps of the developed thin-film solar cell processing method. The GaAs substrate is depicted in blue in (a)-(c) until its removal. The solar cell inverted epitaxy is shown in orange atop the GaAs substrate in the beginning of the process. The Si-wafer is depicted in grey from it appears in the front side metallization (b). The indium foil for soldering (c) is represented in purple. The photoresist used in the photolithography (e) and (f) is depicted in green. The front contact deposited by electroplating of gold (f) is shown in yellow. Finally, the thin gold wires for connecting the solar cell and the PCB (light-blue) in (h) are represented in yellow, the external wires are depicted in two colors, black and red.

4.3 Characterization of the processing method

We have described the steps of our processing method in the previous section. We will not analyze in depth some of them, such as, chemical processes, photolithography techniques and thermal evaporation, since they are well known in processing solar cell devices. On the contrary, we will focus on some practical details of the processes that have been specifically developed in the framework of this Thesis. These processes are the soldering in a vacuum chamber, the substrate removal and the electroplating of the front metal gold.

4.3.1 Soldering in vacuum

The soldering of the solar cell to the Si wafer using an indium foil is carried out in a vacuum chamber. The vacuum chamber is a custom-built equipment which layout is sketched in Figure 4.3 (a). The hotplate is located inside the chamber and its temperature is set by the controller (located in the right part of this front view). The faucet at the left part allows the flow of nitrogen in order to get a controlled atmosphere inside the chamber. Details of the vacuum chamber are shown in Figure 4.3 (b) and (c). In these pictures it can be seen the stack (Si wafer+indium foil+solar cell) under a weight for making extra pressure to assure the bond, and with the glass cover. The indium foil was the optimum choice for soldering. Previously, we tried manually spreading melted indium from a lingot and the result was a non-uniform deposition of the solder between the solar cell that the Si wafer that damaging the ended devices.

Once the soldering is completed, the solar cell is bonded to the Si wafer, which will act as the new support after the GaAs substrate removal. An example of a soldered stack is shown in Figure 4.4.

4.3.2 Substrate removal process

The substrate removal consists of the two-step etching process described previously. The explanation about why the substrate removal consists in a two-step etching lies in the

(a)

(b)

(c)

Figure 4.3: Pictures of the vacuum chamber used for soldering the solar cell stack to a Si wafer. (a) The complete custom-built equipment. In (b) the vacuum chamber is shown opened, with the stack (Si wafer+indium foil+solar cell) and the external weight for making extra pressure to assure the bond. In (c) it is displayed the vacuum chamber with its glass cover.

Figure 4.4: Detail from a soldered solar cell stack with the indium foil.

Figure 4.5: Picture of the state of one sample after having completed the substrate removal process. As it can be seen from the homogeneous flat surface, the surface does not present any air bubble in between the metals, which confirms that the soldering has been suitably done. It should be noticed that there is a small overetched zone, which, however, will not impact the subsequent processing steps.

fact that SEL-1 is made of AlAs. In order to etch the 360- μm GaAs substrate, we need a fast etching, such as $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ (1:1), which etchs the GaAs substrate at a rate of 5-10 $\mu\text{m}/\text{min}$. However, this NH_4OH -based etch is not selective to AlAs, so we have to stop it etch before SEL-1 is reached. At this point we must continue with an AlAs-selective etching, consisting of citric acid: H_2O_2 (5:1), much slower (~ 0.1 $\mu\text{m}/\text{min}$) than the NH_4OH -based etching.

A bare semiconductor device structure of 1.7- μm thickness after removal of the substrate is shown in Figure 4.5. The flat aspect of the epitaxial surface indicates the success

Figure 4.6: Pictures showing bad results after removal of the substrate. (a) is an example of overetching and non-uniform etching. (b) is an example of air bubbles in between the sample and the support, including the soldering indium. In (c) both air bubbles and non-uniform etching can be appreciated. (d) it is an example of the use of spreaded indium from ingot.

of the soldering process. Nevertheless, there is a little overetched zone which, however, does not affect the subsequent processing steps.

Several samples were partially overetched by the first NH_4OH -based etching. As a result, controlling the etching rate was too difficult, as well as its uniformity. Furthermore, the quality of the solder is not appreciated until the substrate has been completely etched. It happened that, sometimes we obtained samples properly etched but with some air bubbles forming in-between the metals. These unsuccessful results, including those from the use of spreaded melted indium from ingot, are shown in Figure 4.6.

4.3.3 Electroplating set-up

An electroplating set-up has also been developed out in this Thesis. The complete set-up for the electroplating process is shown in Figure 4.7. This set-up for depositing gold consists of the following elements:

- a gold electroplating solution for electronic applications, Transene Sulfite Gold TSG-250. The operating conditions from the datasheet are shown in Table 4.1.
- the anode is a platinezed electrode.
- the cathode is the sample itself.
- a power supply, in this case a Keithley™ 6221, DC and AC current source.
- a hotplate and stirrer, which serves at the same time for controlling the temperature (by using a thermometer) of the gold sulfite as well as for stirring it to assure its uniformity.
- other elements, such a chronometer, a voltmeter (for checking the operating voltage), and some glasses of water.

The main elements of the system are indicated with labels in different colors. A more detailed picture of the system is shown in the Figure 4.8, where the glass with the gold sulfite, the electrodes, and the sample can be appreciated.

In a electroplating process there are some parameters that have to be controlled because they affect to the features of the metal to be deposited, such as the deposition rate, the thickness of the deposit and the roughness of the metal. In our case, we have controlled the temperature of the electrolyte, the current density that flows through the gold electrolyte and the stirrer speed. The pH of the electrolyte can also be monitored, but in this first set of trials, we decided not to do it for simplicity (because we want to optimize firstly the current density required). The electroplating parameters were chosen to be within the ranges indicated in the gold-sulfite datasheet: electrolyte temperature

Figure 4.7: Electroplating set-up used in our processing method. The different elements that are part of the set-up are shown and some of them are indicated by pointing arrows. Other required elements are a chronometer (for controlling the etching time), a voltmeter (for checking the voltage applied to the system) and a couple of glasses of water (for rinsing the sample after the depositing).

Figure 4.8: Detail of the electroplating set-up. The sample (with a crocodile clip as anode) and the platinum cathode are inside the electrolyte. It can be appreciated that some gold has already been deposited on the sample, following the photolithography pattern.

Table 4.1: Operating conditions of the Transene Sulfite Gold TSG-250 for electroplating.

Temperature	43°C-71°C
Current Density	1-8 mA/cm ²
Agitation	100 % efficiency-vigorous
pH	6.0-7.0
Tank	Polypropylene, glass, fiberglass
Gold Content	1 troy ounce/gallon

around 60°C, the electrical current is fixed by the current source⁵, and the stirrer is set in such a position that assures the efficient stirring of the sulfite.

The main advantages of the electroplating process relies in its versatility, flexibility and ease of use. Very thick metal layers can be deposited by electroplating what does not impose any significant restriction for the size of the samples. The assembly of the set-up is much simpler and less expensive than other metalization techniques, such as Joule effect or e-beam evaporation. In particular, the electroplating setup does not require a vacuum chamber. Furthermore, the use of electroplated contacts reduces the processing time of the devices, being 5-10 min the total time of the eletroplating process (depending on the deposition rate), while the thermal evaporation process usually takes around 2 hours⁶. However, we have not carried out a deep study about the characteristics of the electroplated gold, because our intention in this first attempt was to obtain an operative device.

4.3.4 Fabricated thin-film solar cells

To conclude this section we will present some images of solar cells fabricated following the previously described processing method. We will also introduce some encountered drawbacks of the process.

⁵The datasheet indicates the range within the current density must be. The electrical current, which is applied, is calculated by multiplying that current density and the measured area of the sample.

⁶In thermal evaporation, vacuum of the chamber has to be done and it takes around 1.5 hours.

Figure 4.9: Pictures of the completed device after the fabrication process. (a) sample S1 after processing into solar cells and before wiring. In (b) the manual process of wiring the solar cells with silver epoxy is shown (picture taken with the optic microscope of the wire-bonder). Image (c) shows the solar cell with the thin gold wires fixed with the silver paste. Picture (d) shows the solar cells together with the copper wires that are necessary for connecting them to the characterization set-ups.

Figure 4.9 shows some pictures of completed devices after the fabrication process. Sample S1 before wiring is shown in Figure 4.9 (a). A thin gold wire bonded to the metal grid with silver epoxy and the external copper wires soldered on PCB can be observed in Figures 4.9 (c) and (d). The two big dark spots on the upper part of the device are silver epoxy manually deposited. The small dark spot at the center of the device is a surface defect, probably originated during the soldering in vacuum step. The copper wires offer to us the possibility of characterizing the solar cells without using probes that could break the samples.

Figure 4.10: SEM image of a processed device as in step (d) of Figure 4.2.

Scanning electron microscopy (SEM) images were acquired by the Institute of Nanoscience of Aragon (INA) at the University of Zaragoza (Spain) and the National Center for Electron Microscopy at the University Complutense of Madrid using two different microscopes. Figure 4.10 was acquired using an SEM Inspect™ F50 operated at 15 keV and different magnifications. Figure 4.11 was carried out in a JEOL JSM-6335F and it was recorded working at an acceleration voltage of 20 kV and a working distance of 15 mm at different magnifications.

Figure 4.10 shows a SEM image of one of the solar cells after removal of the substrate (step *d* in Figure 4.2). The indium layer can be seen between the epitaxial solar cell (top thin dark region) and the silicon wafer (bottom region). The thickness of the indium-layer after soldering and removal of the substrate was approximately 30 μm .

Figure 4.11 shows a SEM image of a completely processed device before wiring (step *g* in Figure 4.2). This picture displays both the front and back contacts of the solar cell through the front metal grid and the indium layer, respectively. The epitaxial thin film, too thin to be properly appreciated in this image, is indicated.

Figure 4.11: SEM image of a processed device as in step (g) of Figure 4.2.

4.4 Optoelectronic characterization of the solar cells

For PC and EQE measurements, samples were mounted on a copper disk and placed in a closed-cycle helium cryostat. Light from a halogen lamp was diffracted with the aid of a Cornerstone 260™ 1/4 m monochromator M-74100 Newport® and chopped. The PC detection was done using conventional lock-in techniques (Stanford Research Systems® DSP Lock-in Amplifier, Model SR830) and a low-noise current preamplifier (Stanford Research Systems®, Model SR570).

Current density-voltage ($J - V$) measurements were performed under approximate AM1.5D solar spectrum and standard measurement conditions ($T = 25^\circ$). The spectrum was obtained by filtering light from a xenon lamp with appropriate AM1.5D filters.

4.4.1 Low temperature photocurrent measurements

To verify the validity of our processing method to perform low temperature characterization, we have measured the spectral PC and EQE of the thin-film AlGaAs samples

Figure 4.12: Photocurrent of sample S1 as a function of the excitation photon energy, at different temperatures. The theoretical bandgap of the $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ at each temperature is indicated with vertical dashed lines.

at different temperatures ranging from 300 K to 20 K. PC results for S1 are shown in Figure 4.12. EQE results for S2 are shown in Figure 4.13. The theoretical bandgap of $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ at each temperature, based on the formulae by Vurgaftman and Meier [Vur 01], is indicated as vertical dashed lines in the graphs. We can see that, in both samples and for all temperatures, PC is produced when the samples are illuminated with supra-bandgap light. From the measurements we conclude that the sample is operational at the intended temperature since, in particular, the experimental absorption threshold energies match the theoretical ones determined by the bandgap. For the case of S2, the sub-bandgap response of the solar cell can be measured even at 300 K. This response is attributed to the absorption of light in the InAs QDs. Furthermore, Fabry-Perot oscillations, due to the reduced thickness of the devices, can be appreciated in the sub-bandgap EQE of S2. In the supra-bandgap range of the EQE, the high absorptivity of the AlGaAs prevents Fabry-Perot effects. At 195 K the sub-bandgap EQE of S2 is strongly reduced, due to the inhibition of the thermal escape of photocarriers out of the QDs, as expected

Figure 4.13: *EQE* measurement of sample S2, as a function of the excitation photon energy and at different temperatures. The theoretical bandgap of $\text{Al}_{0.35}\text{Ga}_{0.65}\text{As}$ at each temperature are indicated with vertical dashed lines.

in a high-bandgap quantum dot solar cell, [Ant 10a, Ram 12]. Therefore, our processing method has enabled us to verify two key aspects of QD solar cells (sub-bandgap PC and inhibition of thermal carrier escape) for the first time in thin-film devices.

The relatively low value of the supra-bandgap *EQE* of S2 is due to a non-optimized layer structure, the lack of anti-reflective coating, and increased carrier recombination introduced by the QDs. However, it must be noted that the results do not show sample degradation at low temperature due to mechanical stress, as it was intended by the use of indium for the soldering. In fact, at 100 K and below, the measured PC of S1 increased in the high-energy photon range, resulting probably from an increase in the lifetime of minority carriers in the emitter of the solar cell. These results prove the adequacy of our processing method for performing low-temperature characterization on thin-film QD-IBSC based on III-Vs devices.

Figure 4.14: Current density-Voltage characteristic at room temperature of S2.

4.4.2 Room-temperature current-voltage measurements

The room temperature $J - V$ characteristic for S2 is shown in Figure 4.14. The QD solar cell exhibits an open-circuit voltage (V_{OC}) of about 0.52 V. This value is low compared to high-performance AlGaAs solar cells with similar Al content [Tak 01], which exhibit a V_{OC} greater than 1.3 V. This large voltage drop is attributed to a large increase in the solar cell non-radiative recombination resulting from the inclusion of the dots, as it is common in QD solar cells [Luq 04, Lam 16]. The J_{SC} is 2.6 mA/cm², in agreement with the measured QE , previously described. Despite the poor performance of the QD devices, the $J - V$ result proves that the fabricated thin-film QD solar cells are operational.

4.4.3 Limitations

Some of the thin-film solar cells exhibit, however, degraded $J - V$ characteristic. For example, the $J - V$ curve with a solar cell of structure S1 is depicted in Figure 4.15 (a) and the $J - V$ curve of a QD solar cell of structure S2 is depicted in Figure 4.15 (b). These curves exhibit rectifying characteristic at low-current densities. The rectifying

(a)

(b)

Figure 4.15: Examples of degraded current density-voltage characteristics at room temperature of (a) S1 and (b) S2. The $J - V$ characteristics of these samples reflect a degraded performance probably caused by the appearance of a Schottky contact between the semiconductor and the metal. This non-optimum contact might come from the electroplated gold and the absence of annealing process.

characteristic might be due to the formation of a Schottky contact [Lep 68] between the semiconductor solar cell and the gold top contact. A satisfactory ohmic contact allows current to circulate across the device with negligible voltage drop (compared with voltage drop across the active region of the device). Conversely, Schottky contacts present a barrier for the current flow, which results in a degraded photovoltaic performance. In the samples, the n-contact GaAs layer of the epitaxial structures have been grown with a doping level of $3 \times 10^{18} \text{ cm}^{-3}$, which is a low doping level to achieve an ohmic contact for GaAs. Unfortunately, we cannot thermally anneal the front contact due to the presence of the indium layer. These reasons justify the n-type contact atop the solar cells might be a Schottky contact. This represents a limitation of our processing method. In future works, we should develop a processing method which allows us to anneal the top contact of the solar cells.

Another limitation in our method is related to the bonding of the thin wires to extract the electrical current. At the present stage, this bonding has to be manually done –at least for the very thin devices– in order not to degrade the samples.

At this point, we cannot demonstrate that the absorption of light in sample S2 (InAs/AlGaAs thin-film QD-IBSC) has been improved by the back reflector. This back reflector should provide a two-fold increase in the optical length of the absorbing layers. To demonstrate it, we would need, for comparison, an additional solar cell structure for fabricating and characterizing a benchmark AlGaAs device, in which the GaAs substrate would remain.

4.5 Conclusions

In this work we have presented and demonstrated a substrate removal processing method for III-V thin-film solar cells. The main general conclusions that we can abstract from it are summarized in the following points:

- Our method is compatible with low-temperature characterization of thin-film III-V solar cells. The key aspects of this method are: (1) the use on In (high thermal

conductivity and low tensile strength), (2) the soldering under vacuum (to avoid the formation of air bubbles), and (3) the use of a conductive flat support (to allow heat dissipation).

- Using this method, we have soldered 1.74- μm thick inverted AlGaAs solar cells onto a flat silicon support. Through photocurrent measurements, we have demonstrated, for the first time to our knowledge, efficient heat dissipation in the 20-300 K range using thin-film solar cells soldered to a silicon wafer. Moreover, the photocurrent results do not show any sign of strain-induced degradation at low temperatures.
- We have fabricated successfully operative thin-film QD-IB AlGaAs-based solar cells. Through temperature-dependent (300-195 K) EQE measurements, we have demonstrated sub-bandgap photocurrent and inhibition of thermal carrier escape in QD samples containing one layer of InAs/AlGaAs QDs in which the substrate has been removed.

Chapter 5

Impact of the spectrum in annual energy efficiency of MJSC

5.1 Introduction

In the previous Chapter, this Thesis has dealt with several approaches for improving the efficiency of IBSCs. For example, in Chapter 2, we studied how to improve the absorption of sub-bandgap photons in InAs/AlGaAs QD-IB devices by texturing the GaAs substrate. In Chapter 4, we presented a new substrate removal processing method compatible with low-temperature characterization, which might be applied to QD-IBSCs implemented with III-Vs semiconductor materials.

5.1.1 Description of MJSC systems

As mentioned in Chapter 1, MJSCs are one of the concepts to improve photovoltaic conversion efficiency. MJSC is the most advanced concept among those defined as “third generation solar cells” MJSCs have the potential to exploit better the solar spectrum than single gap solar cells. They are made of sub-cells piled up in decreasing order of energy bandgap. The most energetic photons are absorbed in the first top sub-cells while the ones with lower energy can pass through these high-bandgap subcells, and are

absorbed in the following sub-cells with narrower bandgaps. Consequently, MJSCs take advantage of the absorption of photons in a wider energy range. Additionally, MJSCs reduce thermalization losses. Depending on how the sub-cells are connected, MJSC can be:

- a) Multi-junction solar cell series connected (MJSC-SC), when the anode (cathode) of each cell is connected to the cathode (anode) of the next. Due to this series connection between the cells, the full cell assembly exhibits only two external terminals.
- b) Multi-junction solar cell independently connected (MJSC-IC), when both the anode and the cathode of each cell are accessed independently.

In figure 5.1 an example of a MJSC system is depicted to illustrate the concept. It represents a simple monolithically integrated, two terminal MJSC made of 3 sub-cells semiconductor materials (whose bandgaps are $E_1 > E_2 > E_3$), able each to absorb photons above their bandgap while transmitting lower energetic photons to the next sub-cells. In this monolithic MJSC the internal series connection of the sub-cells is achieved by tunnel diodes¹ [Esa 58, Esa 60]. The ASTM G173-03 [AST 08] reference spectrum (containing AM1.5 direct normal plus circumsolar irradiance) is also represented. This spectrum is the usual standard for concentrating photovoltaics (CPV). The illustration sketches the light absorption of each sub-solar cell of the MJSC stack and how the sub-cells do not absorb photons with energy $\varepsilon < E_G$.

The series connection under the MJSC-SC approach imposes a constraint by which the current flowing through all the sub-cells has to be the same. This restriction makes the maximum power operating point of each cell to depend on each other. In the MJSC-IC approach, the independent connection between the sub-cells eliminates this current constrain and causes the efficiency of the MJSC-IC to be higher than the efficiency of

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¹In MJSC-SC a tunnel diode allows current to pass due to its low resistance. The operating point of the tunnel diodes imposes a limitation to the performance of the MJSC-SC stack. Tunnel diodes also absorb some of the light reaching them. They also exhibit an operation range with negative resistance, which is applied to others electronic devices.

Figure 5.1: Simplified scheme of a MJSC system. It depicts a monolithic approach made of semiconductor materials with different band-gap energies. The AM1.5 direct normal plus circumsolar irradiance corresponding to the ASTM G173-03 reference spectrum is also depicted. The MJSC stack depicted consists of three sub-cells with bandgaps $E_1 > E_2 > E_3$. The figure schematically illustrates absorption and transmission processes of photons that take place in a MJSC. In this configuration, photons are absorbed in the sub-cell with the largest possible bandgap, where they can be more efficiently harvested. Photons with energy $\varepsilon < E_3$ are not absorbed by the MJSC stack. The system illustrated corresponds to MJSC-SC with two electric terminals.

the MJSC-SC although at the cost of introducing the aforementioned terminals to each sub-cell.

5.1.2 Aim of this Chapter

In order to maximize the photovoltaic conversion efficiency of MJSCs, the values of the bandgaps of the solar cells have to be optimized. This optimization has already been carried out in the past by several authors [Mar 96, Gre 01, Kur 07, Kur 08, DeV 80, Bre 08, AST 92, Abb 11, Gre 12]. However, we need to carry out this optimization process again due mainly to the fact that not all the values that we need for our calculations are available and, often, they have not been calculated for the most recent solar ASTM G173-03 spectrum standards. The results of this revised and completed optimization are provided in Section 5.2.

MJSC-IC exhibit lower sensitivity to changes in the solar spectrum than MJSC-SC what impacts on the annual energy production of the cells. Furthermore, given the fact that optimized MJSC-IC are more efficient than MJSC-SC, it is worth calculating the amount of additional annual energy that it is possible to produce with photovoltaic systems based on MJSC-IC with respect to those based on MJSC-SC. Similar studies were done for 500 suns and specific locations [Dim 10]. Our study is extended to MJSC-IC and for 1 sun, 500 suns, and maximum concentration at the time it generalizes the theory to consider the air mass and the geographical latitude. This study will be detailed in Section 5.3.

In Section 5.4 we will analyze the impact on the efficiency of the annual energy production of MJSCs due to the limited energy harvest from CPV systems².

5.2 Revision of the limiting efficiency of MJSCs

Figure 5.2 (a) illustrates the MJSC-SC system and Figure 5.2 (b) the MJSC-IC system used for this part of the work. The systems are made of N cells ordered by decreasing

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²CPV systems work under concentrated sunlight and they use lenses and/or curved mirrors to focus direct sunlight onto small highly efficient but expensive solar cells with the aim of reducing the total cost.

Figure 5.2: Diagram of the MJSCs systems studied in this work. Selective mirrors have been placed between each solar cell to prevent radiative coupling between the cells. The last cell in the stack also contains a back reflector. In (a) each solar cell of the series system is connected to the following one. In (b) each cell is independently connected to the others.

gap. The cell $n = 1$ is the solar cell with the lowest bandgap. Figure 5.2 (a) depicts a MJSC-SC that, as anticipated in the introduction, exhibits two electric terminals for the whole stack. E_n indicates the energy bandgap of cell n . Solar cells are assumed to absorb all the light they receive that is characterized by photon energy above this gap and they are able to transmit photons with energy below their bandgap. The independently connected system (MJSC-IC) is similar, but two independent electric terminals are extracted from each cell. Later on will be discussed that, in the limit of infinite cells, the limiting conversion efficiency for both MJSC-SC and MJSC-IC is the same.

5.2.1 The detailed balance framework

In order to calculate the limiting efficiency of the systems, each cell is assumed to have a selective reflector attached to its rear part that prevents radiative coupling between the cells. By doing so, photons emitted by cell n through its rear side are reflected back towards the same cell and photons emitted by cell $n + 1$ from its front side are reabsorbed by cell $n + 1$. This approach is known to lead to the maximum efficiency. The theory related to the calculations of the efficiency limit of these multigap systems was described in [Mar 96] and we want to expound it briefly here to give to the reader the general framework for understanding the calculations and the results. The calculations are based on the detailed balance theory formulated by Shockley-Queisser [Sho 61].

The main assumptions made, regarding the operation of the cell, are:

- a) Only radiative recombination processes take place. Each photon is assumed to produce only one electron-hole pair when absorbed and each electron-hole pair produces only a photon when recombined.
- b) Carrier mobility is assumed to approach infinity so ohmic losses are neglected.
- c) The absorptivity and the emissivity are equal. In addition, photon recycling [Mar 97] effects have been taken into account.
- d) The cells are supposed to have a perfect back reflector.

Figure 5.3: The ASTM G173-03 reference spectra, including the AM1.5 direct plus circumsolar spectrum (orange), which is used in CPV, and the AM1.5 global spectrum (green), which is used in 1 sun calculations.

- e) The approach to maximize the operation of the MJSC consists in achieving the maximum power point (MPP) for each individual cell in the IC-approach and for the whole system in the SC-approach.
- f) To achieve the maximum efficiency, the bandgap of the cells require optimization.

These are the general key-points that are sufficient to comprehend what follows. For the optimization and the calculations we have have used the ASTM G173-03 reference spectra.

5.2.2 The limiting efficiencies for ASTM G173-03 reference spectra

The spectra used in the calculations is this work are the ASTM G173-03 reference spectra, as shown in Figure 5.3. The AM1.5 global irradiance has been used for the case of 1 sun and the AM1.5 direct normal plus circumsolar³ irradiance has been used for the

³The circumsolar irradiance is the diffuse irradiance in the immediate vicinity of the sun and it is assumed to be within an opening half-angle of 2.5°.

Figure 5.4: Flow chart of the optimization process for a MJSC of n sub-cells.

(a)

(b)

Figure 5.5: Maximum efficiency as a function of the number of solar cells: (a) for independently connected cells and (b) for series connected cells in the tandem system. The broken lines are a guide to the eye.

concentration cases (500 suns and maximum concentration). When different values of the relative air mass (or simply air mass (AM)) have been needed, the spectrum has been calculated making use of SMARTS2 v.2.9.2 simulation software [Gue 95] by keeping constant all the parameters characterizing ASTM G173-03 (humidity, aerosol, etc.) but changing the value of AM. For reference, we shall mention that the integrated (by trapezoids) power for the AM1.5 direct normal plus circumsolar irradiance conditions results in 901 W/m² and, for AM1.5 global irradiance conditions, results in 1013 W/m² (which is the spectrum used when we will later refer to the 1 sun case).

Figure 5.4 shows the flowchart of the optimization process for the MJSC systems. Initially, the bandgap, $E_{i,0}$, and the operation voltage, $V_{i,0}$, of each individual sub-cell are set. Our optimization process has consisted in several iterations. We have swept the E_i of each sub-cell (fixing the other ones) and obtaining the MPP ($V_{i,opt}$ and $I_{i,opt}$) until achieving the maximum efficiency for these $E_{i,opt}$ and $V_{i,opt}$ values. Afterwards, we set $E_{i,opt}$ and $V_{i,opt}$, and repeat the process for each sub-cell in the MJSC stack until achieving the maximum efficiency for the whole set of $E_{i,opt}$ and $V_{i,opt}$ values. Once we have got the optimum values of the bandgaps, we calculate the tolerance of these bandgaps to preserve the maximum efficiency within 1 % from the maximum when one bandgap is swept and the others are kept constant.

Figure 5.5 details the limiting efficiencies calculated for these ASTM G173-03 spectra, for the cells assumed at 300 K, up to a system consisting of six cells as well as for the ideal case of a system of infinite cells for the cases of 1 sun, 500 suns, and maximum concentration (46050 suns). The values for the case of MJSC-SC and MJSC-IC are represented in Figure 5.5 (a) and (b), respectively. As we have previously explained, the bandgaps of the cells have been optimized for each case and their values are represented in Figure 5.6 to Figure 5.8. In each figure, part (a) depicts the values for the case of MJSC-SC and part (b) for MJSC-IC. In these figures, bars indicate the tolerance in the value of the optimum gap, as explained before, to preserve the maximum efficiency within 1 % from the maximum when the value of the gap is modified. The values depicted in figures 5.5 to 5.8 are also shown in Table 5.1.

(a)

(b)

Figure 5.6: Optimum gaps as a function of the number of cells in the stack for AM1.5 direct normal plus circumsolar irradiance and 500 suns of concentration; (a) MJSC-IC; (b) MJSC-SC.

(a)

(b)

Figure 5.7: Optimum gaps as a function of the number of cells in the stack for AM1.5 direct normal plus circumsolar irradiance and 500 suns of concentration; (a) MJSC-IC; (b) MJSC-SC.

(a)

(b)

Figure 5.8: Optimum gaps as a function of the number of cells in the stack for AM1.5 global irradiance (1 sun); (a) MJSC-IC; (b) MJSC-SC.

Table 5.1: Optimum efficiency and bandgaps for multigap systems with different number of cells for the AM1.5 direct normal irradiance (for the cases of concentration) and AM1.5 global irradiance (for the case of 1 sun) from ASTM G173-03 reference spectra. The first column refers to the number of sub-cells of the stack. The second column refers to the characteristics of the stack, which are (I) the sunlight illumination concentration (maximum concentration, 500 suns and 1 sun) and (II) the series or the independently connections. The third column and its below sub-columns are the optimum gaps values for each one of the sub-cells of the tandem. The last column is the resulting efficiency.

N	Description	Optimum gaps (eV)						η (%)
		E_1	E_2	E_3	E_4	E_5	E_6	
1	Max. Conc.	1.12	-	-	-	-	-	45.0
	500 suns	1.12	-	-	-	-	-	40.1
	1 sun	1.14	-	-	-	-	-	33.5
2	SC Max. Conc.	0.70	1.44	-	-	-	-	60.2
	IC Max. Conc.	0.70	1.52	-	-	-	-	60.3
	SC 500 suns	0.93	1.57	-	-	-	-	53.4
	IC 500 suns	0.70	1.52	-	-	-	-	53.4
	SC 1 sun	0.93	1.59	-	-	-	-	45.6
	IC 1 sun	0.94	1.65	-	-	-	-	45.9
3	SC Max. Conc.	0.54	1.11	1.69	-	-	-	67.2
	IC Max. Conc.	0.69	1.15	1.81	-	-	-	67.8
	SC 500 suns	0.70	1.18	1.75	-	-	-	60.5
	IC 500 suns	0.69	1.16	1.81	-	-	-	60.8
	SC 1 sun	0.70	1.19	1.77	-	-	-	51.1
	IC 1 sun	0.70	1.18	1.89	-	-	-	51.4
4	SC Max. Conc.	0.51	0.96	1.36	1.87	-	-	72.2
	IC Max. Conc.	0.51	0.94	1.39	2.02	-	-	72.6
	SC 500 suns	0.69	1.04	1.44	1.93	-	-	64.2
	IC 500 suns	0.52	0.94	1.39	2.02	-	-	65.0
	SC 1 sun	0.72	1.11	1.48	1.99	-	-	55.1
	IC 1 sun	0.70	1.12	1.57	2.18	-	-	55.8
5	SC Max. Conc.	0.52	0.82	1.19	1.55	2.02	-	73.8
	IC Max. Conc.	0.51	0.94	1.38	1.81	2.33	-	75.6
	SC 500 suns	0.54	0.92	1.21	1.56	2.03	-	67.0
	IC 500 suns	0.52	0.94	1.38	1.81	2.33	-	68.0
	SC 1 sun	0.69	0.99	1.27	1.63	2.11	-	57.3
	IC 1 sun	0.69	0.98	1.38	1.81	2.40	-	58.3
6	SC Max. Conc.	0.51	0.78	1.05	1.36	1.67	2.12	76.2
	IC Max. Conc.	0.51	0.94	1.33	1.64	2.00	2.48	77.3
	SC 500 suns	0.51	0.78	1.06	1.36	1.67	2.12	68.5
	IC 500 suns	0.52	0.94	1.33	1.64	2.00	2.48	69.6
	SC 1 sun	0.69	0.96	1.19	1.46	1.78	2.23	59.4
	IC 1 sun	0.69	0.96	1.34	1.64	2.02	2.53	59.9

As anticipated, MJSC-IC is more efficient than MJSC-SCs when a finite number of solar cells is considered. The relative difference between the limiting efficiencies of the MJSC-IC and those of the MJSC-SC for maximum concentration varies from 0.1 % to 2.3 %. For a concentration of 500 suns, this relative difference in efficiency varies between 0.4 % to 1.5 %. At 1 sun, the relative difference goes from 0.6 % to 1.6 %. Besides, a comparison between the limiting efficiencies calculated previously with the now obsolete spectra and the revised ones shows, for example, that the revised limiting efficiency for a 4 MJSC-SC results in 55.1 % at 1 sun (while the previous one was 54.0 %) 64.2 % for 500 suns (versus 63.6 %) and 72.2 % for maximum concentration (versus 71.0 %). The limiting efficiency for single gap solar cells at 1 sun has also been calculated by Green [10] for the new ASTM G173-03 standard obtaining two maximum values: 33.8 % for a bandgap of 1.34 eV and 33.6 % for 1.15 eV. Our limiting efficiencies for both bandgaps result in 33.5 % in both cases.

The increase in the photovoltaic conversion efficiency saturates as the number of solar cells in the tandem increases. In fact, the limiting efficiency for both types of MJSCs becomes the same when an infinite number of solar cells is considered, as previously demonstrated in [Tob 02, Bro 02]. For the updated calculations these limiting efficiencies result in: 85.9 % for maximum concentration, 77.9 % for a concentration of 500 suns, and 75.3 % for 1 sun.

Another advantage of the MJSC-IC in comparison with MJSC-SC is revealed by the tolerance of the optimum gaps to achieve the maximum efficiency which is higher for the MJSC-IC case. In addition, the tolerance of the optimum bandgaps to changes in the solar spectrum is also higher in the MJSC-IC than in the MJSC-SC case. Consequently, this higher tolerance allows to choose the potential candidates as semiconductors to make the MJSCs more freely in the case of MJSC-IC than in MJSC-SC.

(a)

(b)

Figure 5.9: Optimum efficiency for maximum concentrated light as a function of the solar spectrum variation for different AM coefficients for the case of: (a) MJSC-SC and (b) MJSC-IC.

(a)

(b)

Figure 5.10: Optimum efficiency for 500 suns of concentrated light as a function of the solar spectrum variation for different AM coefficients for the case of: (a) MJSC-SC and (b) MJSC-IC.

(a)

(b)

Figure 5.11: Optimum efficiency for 1 sun-light as a function of the solar spectrum variation for different AM coefficients for the case of: (a) MJSC-SC and (b) MJSC-IC.

5.3 Annual energy production efficiency

5.3.1 The concept of annual energy production efficiency

In this section we want to proceed with a different concept from the efficiency of the solar cells, which is the annual energy production efficiency (AEE). The AEE is defined as the maximum photovoltaic energy produced by the cells in one year divided by the total energy received from the sun during the year. This efficiency should not be confused with the efficiency of the cell, discussed in the previous sections, which is defined as the ratio between the maximum output power produced by the cell and the power of the input solar irradiance for a given spectrum.

Since the solar spectrum changes along the daytime, in order to calculate the AEE it is necessary to know the efficiency of the solar cells as a function of the AM of the solar spectrum. This efficiency is calculated preserving the value of the gaps of the cells as the optimum ones calculated in Figures 5.6 to 5.8, that is, the ones that are optimum for AM1.5 direct normal plus circumsolar for the concentration cases and AM1.5 global irradiances for 1 sun case, and sweeping the irradiance conditions by changing the AM values. These efficiencies are plotted in Figure 5.9 for the case of maximum concentration, Figure 5.10 for the case of 500 suns, and Figure 5.11 for the case of 1 sun.

In these figures it can be appreciated that while the values of the efficiencies for MJSC-IC are maintained close to the maximum while AM varies, the values of the efficiencies for MJSC-SC rapidly decrease and collapse with the change of the irradiance conditions.

5.3.2 The framework for the annual energy production efficiency

AM values have been correlated with the terrestrial latitude and daytime through the approximation given in [Gre 00]:

$$AM = \frac{1}{\cos(90^\circ - h)} \quad (5.1)$$

Figure 5.12: Geometry of the earth-sun system from the view point of an observer at the position P on earth's surface. This sketch defines all the angles employed to define the sun position.

where h is the solar altitude angle or the solar elevation angle and is calculated, as a function of the time of the day, by means of the formula:

$$h = \sin^{-1}(\sin \phi \sin \delta + \cos \phi \cos \delta \cos \omega) \quad (5.2)$$

where ϕ is the latitude, positive for the Northern Hemisphere, in degrees and δ is the solar declination angle in degrees. These angles are depicted in Figure 5.12, which sketches the geometry of the earth-sun system from the viewpoint at the position P on earth's surface. Angle ω is the solar hour angle in degrees, defined by:

$$\omega = 15(t - 12) \quad (5.3)$$

where t is the time in decimal hours on the 24 hour clock (using Local Apparent Time) converted to hour angle. The hour angle at solar noon is set as zero. The hour angle is set as positive after solar noon and negative before solar noon. For example, 10

AM in terms of hour angle is -30° . And finally, the simplified formula in degrees for the solar declination angle is given by:

$$\delta = \sin^{-1}(0.3978 \sin(j - 80.2^\circ + 1.92 \sin(j - 2.80^\circ))) \quad (5.4)$$

where j is the Julian day number expressed as a day angle in radians (multiplying the Julian day number by 360° and dividing by the mean length of the year, that is, 365.25), and the angles are in degrees. For example, my birthday, which is on 11th August, in terms of day angle is equal to 3.83 radians (or 219.19°).

In our calculations, the value of the AM has been approximated by Equation 5.1:

$$AM = \frac{1}{\cos(90 - h)} = \frac{1}{\cos \theta} \quad (5.5)$$

where $\theta = 90 - h$ is the zenith angle of the sun. This equation assumes that the atmosphere is a flat horizontal layer and can be considered correct within 10% for AM values lower than 15 [Gue 95, Kas 89, Gre 92, You 94] which are the practical values used in this work.

AEE considers the whole amount of energy along the year reaching the MJSC taking into account the spectra for different relative air mass coefficients. In practice, in our calculations, we have taken a maximum value of 20 for the air mass coefficient where the solar irradiance is $133.4 \text{ W}\cdot\text{m}^{-2}$ for the direct normal plus circumsolar spectrum and $155.1 \text{ W}\cdot\text{m}^{-2}$ for the global spectrum. From AM20 to AM38.2 the solar irradiance has been considered negligible in terms of AEE.

5.3.3 Results for the annual energy efficiency

With this knowledge and the values of the efficiency of MJSC vs AM, we can study the ideal performance of MJSC from a different perspective. In this respect, in Figure 5.13 we plot the values of the AEE calculated for a terrestrial latitude⁴ of $\lambda = 40^\circ$ and: (a) Maximum concentration, (b) 500 suns, and (c) 1 sun.

⁴ $\lambda = 40^\circ$ is chosen because corresponds to the terrestrial latitude of our location (Madrid, Spain).

(a)

(b)

(c)

Figure 5.13: Optimum annual efficiencies for stacked tandem systems with series connected and independently connected solar cells for terrestrial latitudes of 40° and illumination conditions of: (a) maximum concentration, (b) concentration of 500 suns, for AM1.5 direct, and (c) 1 sun, for AM1.5 global. The broken lines are a guide to the eye.

As it can be seen in these graphs, MJSC-IC provide higher values of AEE than MJSC-SC for the same number of sub-cells. Moreover, for illustrative purposes, in systems consisting of four solar cells, under illumination conditions of 500 suns of concentration and for $\lambda = 40^\circ$ terrestrial latitude, it is more favourable to evolve from a system with series connection (AEE= 60.3 %) towards one with independently connected cells (AEE= 64.9 %) rather than evolving to a MJSC-SC of five solar cells (AEE= 61.6 %). This advantage increases as the number of cells increases. Hence, for the case of MJSC-SC consisting of five solar cells (AEE= 61.6 %), it is more favourable to progress towards a MJSC-IC consisting also of five solar cells (AEE= 67.7 %) than towards a MJSC-SC of six solar cells (AEE= 63.2 %). Furthermore, this trend is maintained also both under maximum concentration as for 1 sun, as it is shown in the graphs.

The optimum efficiencies of MJSC when the AM changes (Figures 5.9 to 5.11) shows large differences among the results for the same AM value. For example, for the case of maximum concentration and six MJSC-SC at AM20, the efficiency is 5.5 %, while for two MJSC-SC is 33.4 %. Despite these differences the actual solar power involved in AM20 is only $133.4 \text{ W}\cdot\text{m}^2$ (at the zenith) to be compared to $900.8 \text{ W}\cdot\text{m}^2$ of AM1.5D. However, when integrated along the day and the year, the contribution to the annual energy production results in a 6.5 % difference, in other words, these large differences are balanced due to the weight of the spectrum during the day and the year.

5.4 Impact of limited airmass collection

After obtaining and analysing the results of AEE, we want to deepen in our analysis of the ideal performance of MJSC. MJSCs are usually envisaged to be used in CPV systems. However, due to the difficulty of the tracker to follow the sun at low solar altitudes [13], CPV systems are expected to collect energy for solar altitudes greater than 20-30 degrees that correspond in our model to relative air masses lower than 2.5 approximately.

Calculations of the AEE of the MJSCs in the previous section assumed the ideal case in which the cells were able to collect all the sunlight along the daylight, that is, from

Figure 5.14: AM at solar zenith for a terrestrial latitudes of $\lambda = 40^\circ$.

the highest AM values –the solar spectrum at dawn or sunset times– to the lowest AM values corresponding to the solar zenith. The AM value at solar zenith for terrestrial latitudes of $\lambda = 40^\circ$ along the year is depicted in Figure 5.14. In practical concentration systems, however, collecting light at high AM values is difficult due to the limitations of the tracking systems to point towards low altitude angles.

To study the impact of this limitation on the AEE we will assume in this section that the capability of the system to collect sunlight is limited to $AM=AMX$. This AMX value is the limit that we will use now for obtaining the AEE (note that when AMX is equal to AM20, the results are those from the previous section). In this respect, focusing to the case of 500 suns of concentrated sunlight, because it could be the most interesting case in CPV, Figure 5.15 shows a comparison between annual energy efficiencies of MJSC-SC and MJSC-IC taking into account different values of AMX. The results show that the difference between the AEE of MJSC-SC and MJSC-IC increases as AMX increases.

But, regarding the AMX limitation on the AEE, at which point is it worth to evolve from a MJSC-SC to a MJSC-IC made of the same number of sub-cells?

From the results in Figure 5.15, Figure 5.16 (a) illustrates the increment in AEE when considering going from a MJSC-SC system of 3 cells to a MJSC-IC of 3 cells and also to a MJSC-SC system of 4 cells as a function of AMX. As it can be seen, in this case, the MJSC-SC (3 cells) to MJSC-SC (4 cells) approach leads always to higher AEE

Figure 5.15: Annual efficiencies for MJSC independently and series connected for different values of AMX indicated in brackets. The broken lines are a guide to the eye.

increase. The situation changes when we compare going from a MJSC-SC system of 4 cells to a MJSC-SC system of 5 cells or to a MJSC-IC of also 4 cells (Figure 5.16 (b)). In this case, the MJSC-SC (4 cells) to MJSC-IC (4 cells) case results a better option for $AMX > 2.6$, that is, when the concentration system, with its tilt, is capable of collecting daily spectrums characterized by AM higher than 2.6. For that matter, Figure 5.16 (c) depicts an even more favourable approach: going from a MJSC-SC system of 5 cells to a MJSC-SC system of 6 cells never benefits the energy harvesting when it is compared with going from a MJSC-SC system of 5 cells to a MJSC-IC of 5 cells. In short, even when only low AMX is taking account for the operation of the MJSC systems, it is more favourable in terms of AEE going from a 5 MJSC-SC to 5 MJSC-IC.

To put these results into context the AM2.6 spectrum takes place at different hours for each day along the year. As an example, Table 5.2 indicates the solar hour at

Figure 5.16: Comparison of the increment in AEE when considering different number of junctions against AMX. Three comparisons are depicted: (a) going from 3MJSC-SC to 3MJSC-IC and from 3MJSC-SC to 4MJSC-SC; (b) going from 4MJSC-SC to 4MJSC-IC and from 4MJSC-SC to 5MJSC-SC; and (c) going from 5MJSC-SC to 5MJSC-IC and from 5MJSC-SC to 6MJSC-SC. The broken lines are a guide to the eye.

Table 5.2: Solar time at which air mass AM2.6 for terrestrial latitudes of is obtained for several representative dates along the year.

DATE		
03/21	08:05 hrs. AM	03:55 hrs. PM
06/21	06:47 hrs. AM	05:13 hrs. PM
09/21	08:03 hrs. AM	03:57 hrs. PM
12/21	10:35 hrs. AM	01:25 hrs. PM

which the AM2.6 spectrum is obtained for several representative dates (solstices and equinoxes) for a terrestrial latitude.

5.5 Analysis of the AEE results

The efficiency of photovoltaic conversion (for the new ASTM G173-03 reference spectra and different values for the relative air mass) for tandem systems that are made up of one to six solar cells and an infinite number of cells, both series and independently connected, has been revised for the cases of 1 sun, 500 suns, and maximum concentrated light. As expected, the results show that Multi-junction solar cell independently connected have a greater photovoltaic conversion efficiency than the Multi-junction solar cell series connected, as long as the number of cells is finite, and the same limiting efficiency when the number of cells is infinite. In addition, the optimum value of the gaps of the MJSC-IC exhibits a greater tolerance in order to achieve the maximum efficiency than for the MJSC-SC. These results are in accordance with those from the revised literature and, moreover, they complete them in order to fill-in the gaps in the values and for the later analysis of annual energy production efficiency .

We have followed a different approach for studying the performance of the MJSCs through the concept of annual energy production efficiency. The AEE takes into account the maximum amount of energy that an optimized MJSC system can produce along a year. The optimum AEE of MJSC-SC and MJSC-IC consisting of several gaps has also been calculated for 1 sun, 500 suns, and maximum concentration. The results have been exemplified for a terrestrial latitude of 40° .

Due to the removal of the series connection constrain, as expected, Multi-junction solar cell independently connected have shown higher AEE than Multi-junction solar cell series connected for the same number of cells. Furthermore, focusing on four junction tandems (considering that 4-MJSC system is the current field of research in MJSC), MJSC-IC of four gaps have revealed higher AEE than MJSC-SC of five gaps suggesting that going to an approach in which solar cells are independently connected could reveal itself more productive than increasing the number of cells in the system. In addition, our analysis of the AEE taking into account possible limitations in the collection of energy for high AM values has revealed that the advantage persists as long as the system is capable of collecting solar radiation at angles such as the air mass is lower than 2.6. In addition, the results from AEE shows that for 4-MJSC-IC is better than 5-MJSC-SC for $AMX > 2.6$. From this point, either increasing the capability of the CPV systems to collect higher AM or considering an increased number of junctions will be advantageous for the independently connected case. What is more, the results from AEE show that 5-MJSC-IC is better than 6-MJSC-SC for all AMX values, even when only AMX close to 1.5 is considered. This implies that a multi-terminal MJSC approach should be considered as an alternative to 6-MJSC-SC.

Although it is true that a multi-terminal approach faces challenges at device processing and IC design level, it is also true that the monolithic approaches for MJSC-SC face challenges at material level since, each time a new cell is added, the full solar cell stack has to be reviewed, with the consequently conceptual and technological challenge.

The point we would like to defend with this work is precisely that, at present, it is not clear which route is better and that the multi-terminal approach, nowadays perhaps disregarded as an option, might be worthwhile revisiting at the light of the results for the limiting efficiency of annual energy production we have obtained.

5.6 Conclusions

In this Chapter, we have calculated the limiting efficiencies of MJSC-SC and MJSC-IC from one to six sub-cells, as well as for infinite number of cells. In addition, we have

calculated the optimum bandgap for each sub-cell. From these results, we have proposed a different approach for studying the performance of MJSCs through the concept of annual energy production efficiency (AEE). The main conclusions of this Chapter are:

- The limiting efficiency of MJSC-IC is higher than the one of MJSC-SC when considering the same number of sub-cells for the illumination conditions under study (1 sun, 500 suns, and maximum concentration) and the new ASTM G173-03 reference spectra.
- The AEE results show that the multi-terminal MJSC approach should be considered, at least, from 4 sub-cells. 4-MJSC-IC reveals to be more favourable as of $AMX = 2.6$. For that matter, the AEE of 5-MJSC-IC is higher than the one of 6-MJSC-SC for any AMX value.
- In the current state of multi-junction solar cell technology (4-MJSC-SC, with a record efficiency of photovoltaic conversion of 46%), the choice of future technological development (series-connected with increased number of junctions versus independently connected while preserving the number of junctions) is pertinent. The presented results set a new efficiency framework in terms of energy production which can serve as a guidance for moving forward in the aforementioned technological dilemma.

Chapter 6

Conclusions

This Thesis has dealt with the general goal of contributing with advances in different novel solar cells concepts, namely the intermediate band solar cell and the multi-junction solar cell. This Chapter is devoted to summarize the main conclusions derived from the work that has been carried out along this Thesis. We will structure this Chapter by exposing the outcomes from each chapter.

6.1 Implementation of light management approaches in InAs/AlGaAs QD-IB devices

In this Chapter, we have studied the impact of light-trapping techniques applied to QD-IB devices, with the aim of increasing the absorption of photons in the QDs. We have obtained the following conclusions:

We have worked towards the enhancement of the performance of practical QD-IBSCs. One of the issues of the QD-IBSCs is the poor absorption of QDs for producing sub-bandgap photocurrent. We studied in Chapter 2 the impact of light-trapping techniques applied to QD-IB devices, with the aim of increasing the absorption of photons in the QDs. We obtained the following conclusions:

- Surface texturing (via $\text{NH}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$) is an effective means of implement light trapping at sub-bandgaps transition energies in QD-IB devices. Using this approach we have demonstrated absorption enhancement in InAs/AlGaAs QDs. In particular, we have demonstrated for the first time light trapping via surface texturing in QDs in the 0.2-0.65 eV range.
- Two different light-trapping approaches have been studied: texturing+gold and texturing+air. Both schemes result in an increased light absorption. This has been demonstrated by fabricating three different QD-IBSC structures and then applying three kind of textures to them.
- The best results have been obtained by combining the self-organized texturing of the S-I GaAs substrate of the InAs/AlGaAs QD-IBSC with air, instead of a back gold reflector. From the $J - V$ characteristics, the $J_{\text{SC,sub-GaAs}}$ values of the $1 \times \text{QD-layer textured+air}$ Sample is 46 % greater than the corresponding values of the non-textured cases polished one. For the case of $10 \times \text{QD-layer textured+air}$ Sample the relative increment is around 52 % greater than for the non-textured case. When the textured+gold samples are considered, the relative increment is negligible.
- The implementation of surface texturing to InAs/AlGaAs OTIPs improves their response to the IR. We proved it through TPPC measurements. The spectral response of the devices (3-5 μm) supports the use of QD-based OTIPs in optical communications through the atmosphere.

6.2 Demonstration of two-photon photovoltage in QD-IBSC

Regarding the topic of IBSCs, we extend the characterization of QD-IBSCs in Chapter 3. We have studied the increase in V_{OC} in QD-IBSCs by means of two-photon sub-bandgap illumination. In GaSb/GaAs QD-IBSCs, the addition of a second photon beam

of photons with energy $E_H < \varepsilon < E_L$, produces an increase in V_{OC} with respect to illumination only with photons of energy $E_G < \varepsilon < E_H$. This two-photon photovoltage phenomenon represents a key demonstration in IBSCs which had been elusive until now.

We have correlated theoretically the generation of TPPV and the production of TPPC. We have verified qualitatively and empirically this correlation. Theoretically, the production of TPPC should be accompanied by the generation of the TPPV. In the experiments one photon had constant energy $h\nu > E_H$ and the other variable energy $h\nu \geq E_L$. Surprisingly, when the energy of the latter photon was E_L , the production of TPPC is not accompanied by the generation of TPPV. This result is still under study.

6.3 Development of a substrate removal processing method for III-V solar cells compatible with low-temperature characterization

In Chapter 4 we presented and demonstrated a substrate removal processing method for III-V thin-film solar cells. This method was compatible with low-temperature characterization. In addition, the method is suitable to QD-IBSCs based on InAs/AlGaAs materials. The main general conclusions that we can abstract from it are summarized in the following points:

- Our method is compatible with low-temperature characterization of thin-film III-V solar cells. The key aspect of this method are: (1) the use on In (high thermal conductivity and low tensile strength), (2) the soldering under vacuum (to avoid the formation of air bubbles), and (3) the use of a conductive flat support (to allow heat dissipation).
- Using this method, we have soldered 1.74- μm thick inverted AlGaAs solar cells onto a flat silicon support. Through photocurrent measurements, we have demonstrated, for the first time to our knowledge, efficient heat dissipation in the 20-300 K range using thin-film solar cells soldered to a silicon wafer. Moreover, the

photocurrent results do not show any sign of strain-induced degradation at low temperatures.

- We have fabricated successfully operative thin-film QD-IB AlGaAs-based solar cells. Through temperature-dependent (300-195 K) EQE measurements, we have demonstrated sub-bandgap photocurrent and inhibition of thermal carrier escape in QD samples containing one layer of InAs/AlGaAs QDs in which the substrate has been removed.
- We think that the presented method can be useful for the community researching on concentrator thin-film solar cells based on nanostructures (quantum dots and quantum wells) as well as other thin-film technologies.

6.4 Impact of the spectrum in the annual energy efficiency of MJSC

Finally, the last part of this Thesis seeks to expand the understanding of MJSCs and multi-terminal solar cells by providing a wider perspective to analyze their efficiency and performance. In this respect, in Chapter 5, we calculated the limiting efficiencies of MJSC-SC and MJSC-IC from one to six sub-cells, as well as for an infinite number of cells. In addition, the optimization of the MJSC systems has given the optimum bandgap for each sub-cell. From these results, we proposed a different approach for studying the performance of MJSCs through the concept of annual energy production efficiency. In this section, we summarize the derived conclusions from the work that has been carried out and has been presented in Chapter 5:

- The limiting efficiency of MJSC-IC is higher than the one of MJSC-SC when considering the same number of sub-cells for the illumination conditions under study (1 sun, 500 suns, and maximum concentration) and the new ASTM G173-03 reference spectra.

- We made a comparison between series-connected and independently-connected ones in terms of AEE. Due to the removal of the series connection constrain, MJSC-ICs also show higher AEE than MJSC-SCs for the same number of cells.
- The AEE results show that the multi-terminal MJSC approach should be considered, at least, from 4 sub-cells. 4-MJSC-IC reveals to be more favourable as of $AMX = 2.6$. For that matter, AEE for 5-MJSC-IC is higher than 6-MJSC-SC for any AMX value.
- In the current state of multi-junction solar cell technology, the choice of future technological development (series-connected with increased number of junctions versus independently-connected while preserving the number of junctions) is pertinent. The presented results set a new efficiency framework in terms of energy production which can serve as a guidance for moving forward in the aforementioned technological dilemma. It might be more advantageous to take more terminals in a four junctions solar cell rather than to go to five junctions or six junctions solar cells connected in series. We consider that the series connection option is a very demanding technology in terms of new materials, which have to be grown with some degree of lattice matching with each other and, in addition, imply re-designing the full solar cell stack.

Chapter 7

Recommended future works

The work done in this Thesis opens up new lines of work to be explored in further research.

- From the work carried out with self-texturing of GaAs in InAs/AlGaAs QD-IBSCs we propose the following assignments:
  - We have measured the photocurrent response of the $10\times$ QD-layers samples under IR illumination. We have obtained a trend in the results: the self-texturing followed by air benefits the sub-bandgap absorption in the QDs. However, due to the amount of structural defects that are present in the epitaxies and to verify this trend, we should measure the photocurrent response of $1\times$ QD-layer samples under IR illumination the sub-bandgap range to ascertain the trend of the results from the $10\times$ QD-layers samples.
  - Once the self-texturing of the GaAs surface in the devices has proven itself beneficial to the sub-bandgap photon absorption, we aim to incorporate other approaches for texturing QD-IBSC, such as incorporating a layer of TiO_2 microparticles, which have a good diffuse reflection in the IR range of interest (700-5000 μm), on the rear surface of the GaAs substrate.

- To achieve an extensive understanding of the light-trapping phenomenon in QD-IBSCs, we should study theoretically the absorption properties of textured QD-IBSC.
- In Chapter 3, we have measured TPPV in GaSb/GaAs QD-IBSC. The TPPC and TPPV are correlated for all the energy range except for the range $\varepsilon \approx E_L$, where TPPC production is not accompanied by TPPV generation. The reasons for this are at this moment unclear. We should extend our research to understand it.
- In this Thesis we have proposed a substrate removal processing method to fabricate semiconductor thin-film solar cells which is compatible with low-temperature characterization. Future lines of work would include:
  - Fabricating an additional *thick* InAs/AlGaAs solar cell structure (in which the GaAs substrate is not removed) as reference to compare the performance of the *thin* InAs/AlGaAs QD-IBSC. The *thick* InAs/AlGaAs reference solar cell should be an upright-structure.
  - Proceed with light-trapping techniques in thin-film QD-IBSC, such as incorporating a textured layer of semiconductor on the back side.
- In the last part of this Thesis we have dealt with the concept of annual energy production efficiency of MJSCs up to six junctions and we have achieved interesting conclusions when two-terminals system and multi-terminals system are compared. However, we should extend this study to more-than-six junctions MJSC systems for a better and more complete understanding of these systems.

Publications related with this Thesis

Publications in peer-reviewed international journals

1. I. Ramiro, J. Villa, P. Lam, S. Hatch, J. Wu, López, E., E. Antolín, H. Liu, A. Martí, and A. Luque. “Wide-bandgap InAs/InGaP quantum-dot intermediate band solar cells”. *IEEE Journal of Photovoltaics* (Impact Factor 3.712, Q1, Applied Physics, Materials Science). Vol. 5, No. 3, pp. 840-845, 2015.
2. J. Villa, I. Ramiro, J. M. Ripalda, E. Antolín, I. García, and A. Martí. “A substrate removal processing method for III–V solar cells compatible with low-temperature characterization”. *Materials Science in Semiconductor Processing* (Impact factor 2.359, Q2, Applied Physics, Materials Science). Vol. 63, pp. 58-63, 2017.
3. J. Villa and A. Martí. “Impact of the spectrum in the annual energy production of multi-junction solar cells”. *IEEE Journal of Photovoltaics* (Impact Factor 3.712, Q1, Applied Physics, Materials Science), DOI 10.1109/JPHOTOV.2017.2717038.

Contributions to international conferences

1. J. Villa and A. Martí, “Impact of the spectrum, location and interconnection between solar cells in the annual production of photovoltaic energies in photovoltaic concentration systems,” *IEEE 43rd Photovoltaic Specialists Conference (PVSC), 2016*, pp. 0574-0576, 2016.

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