UNIVERSIDAD POLITÉCNICA DE MADRID

**ESCUELA TÉCNICA SUPERIOR
DE INGENIEROS DE TELECOMUNICACIÓN**

TESIS DOCTORAL

**RESEARCH ON INTERMEDIATE BAND SOLAR CELLS AND
DEVELOPMENT OF CAPACITIVE TECHNIQUES FOR THEIR
CHARACTERIZATION (INVESTIGACIÓN EN CÉLULAS
SOLARES DE BANDA INTERMEDIA Y DESARROLLO DE
TÉCNICAS CAPACITIVAS PARA SU CARACTERIZACIÓN)**

Esther López Estrada
Licenciada en Ciencias Físicas

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**Instituto de Energía Solar
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AUTORA: Esther López Estrada
Licenciada en Ciencias Físicas

DIRECTOR: Antonio Martí Vega
Doctor en Ciencias Físicas

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Tribunal nombrado por el Magnífico y Excelentísimo Sr. Rector de la Universidad Politécnica de Madrid.

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A mi familia,
por su ejemplo, su apoyo y su cariño.

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Resumen

Esta Tesis contribuye al desarrollo de las células solares de banda intermedia (IBSCs). La eficiencia límite de una IBSC es del 63,2% bajo unas condiciones de iluminación específicas (la iluminación correspondiente a concentrar al máximo la luz recibida por el Sol, suponiendo que éste es un cuerpo negro a 6000 K). Esta eficiencia límite supera la de una célula solar convencional de un solo gap (40,7%) gracias a la presencia de una tercera banda energética que se suma a las bandas de conducción (CB) y valencia (VB). Esta banda energética adicional se denomina banda intermedia (IB), y está aislada de los contactos metálicos por medio de emisores selectivos al paso de electrones o de huecos. Esta configuración permite que las IBSCs puedan absorber fotones con energías inferiores a la banda prohibida, produciendo una fotocorriente adicional a través de transiciones VB→IB y IB→CB, al mismo tiempo que pueden proporcionar tensiones de salida que exceden el valor de la energía de estas transiciones dividida por la carga del electrón. Estas dos características se conocen como los principios de operación de la IBSC. Los principios de operación han sido demostrados en diferentes tecnologías fotovoltaicas, especialmente en prototipos basados en puntos cuánticos (QDs). Sin embargo, las IBSCs fabricadas hasta el momento aún deben demostrar estos principios en condiciones de operación reales, tales como operar a temperatura ambiente.

En este contexto, nuestro trabajo se centra en estudiar los diferentes enfoques tecnológicos utilizados en la fabricación de IBSCs para así aumentar las posibilidades de obtener dispositivos que operen conforme a la teoría. El objetivo principal de esta Tesis es caracterizar prototipos de IBSCs basados en semiconductores “bulk” que quizá son los menos investigados hasta el momento. En concreto, investigamos prototipos basados en ZnTe:O, Si:Ti y GaAs:Ti. En los prototipos basados en ZnTe:O y Si:Ti, encontramos que las transiciones VB→IB y IB→CB están caracterizadas, respectivamente, por coeficientes de absorción tan altos como 10^4cm^{-1} y secciones eficaces de captura tan bajas como $2 \cdot 10^{-19}\text{cm}^2$. Estas características son adecuadas para la obtención de dispositivos que operen como IBSCs. En los prototipos basados en GaAs:Ti conseguimos probar los principios de operación de las IBSCs. Sin embargo, sorprendentemente, en estos dispositivos los niveles de energía que actúan como una IB están asociados a defectos cristalinos y no de la presencia de átomos de Ti.

En esta Tesis también contribuimos a la demostración de los principios de funcionamiento de las IBSCs en condiciones próximas a las condiciones de operación reales. Prototipos de IBSCs basados en QDs de InAs/Al_{0.3}Ga_{0.7}As y fabricados en la Universidad de Tokio han demostrado la producción de fotocorriente por medio de la absorción de dos fotones, por primera vez a temperatura ambiente. El umbral de absorción de esta fotocorriente se corresponde con las transiciones de menor energía, las

transiciones IB→CB. Esto facilita la demostración de que el voltaje (multiplicado por la carga del electrón) supera el umbral de energía de absorción a temperatura ambiente bajo condiciones de iluminación similares a 0,5 soles.

Con el fin de aumentar la capacidad de investigación del IES-UPM, a lo largo de esta Tesis se implementa un montaje experimental dedicado a la "Espectroscopía de transitorios de niveles profundos" (DLTS). Esta técnica proporciona información acerca de los procesos de recombinación y complementa la caracterización obtenida con técnicas ópticas, que se centran en el estudio de los procesos de generación de pares electrón-hueco.

Abstract

This Thesis is a contribution to the development of intermediate band solar cells (IBSCs). The limiting efficiency of an IBSC is 63.2% under specific illumination conditions (under maximum solar concentration assuming the sun as a black body at 6000 K). The limiting efficiency of IBSCs surpasses the limiting efficiency of conventional single gap solar cells (40.7%) due to the presence of a third energy band, in addition to the conduction band (CB) and the valence band (VB). This third energy band is referred to as the intermediate band (IB) and is isolated from the metal contacts by means of electron or hole selective emitters. This configuration allows IBSCs to absorb photons with energies below the bandgap, generating an additional photocurrent by means of VB→IB and IB→CB transitions and providing output voltages (V) that exceed the energy of these sub-bandgap transitions divided by the electron charge (e). These two characteristics are known as the operation principles of the IBSC. These principles have already been demonstrated in different PV technologies, especially in IBSC prototypes based on quantum dots (QDs). However, IBSC prototypes have not yet fulfilled these principles in real life conditions, such as operation at room temperature.

In this context, our work focuses on the study of different IB technological approaches to increase the possibility of obtaining practical IBSCs. The main objective of this Thesis is to characterize IBSC prototypes that belong to the bulk approach which are perhaps the least investigated technologies. In particular we investigate IBSC prototypes based on ZnTe:O, Si:Ti and GaAs:Ti materials. In IBSC prototypes based on ZnTe:O and Si:Ti, the VB→IB and IB→CB transitions are characterized by absorption coefficients as high as 10^4cm^{-1} and capture cross sections as low as $2 \cdot 10^{-19}\text{cm}^2$, respectively. These features are suitable for IBSC applications. We find the operation principles of IBSCs fulfill surprisingly in IBSC prototypes based on GaAs:Ti, where the energy levels that act as an IB arise from crystalline defects and not from the presence of Ti atoms.

In this Thesis we also contribute to the demonstration of IBSC operation principles under working conditions close to room temperature. IBSC prototypes based on InAs/Al_{0.3}Ga_{0.7}As QDs, fabricated in collaboration with the University of Tokyo, demonstrate for the first time the production of photocurrent by means of the absorption of two-photons at room temperature. The absorption threshold resulting from this two-photon photocurrent corresponds to the least energetic transitions, the IB→CB transitions. This facilitates the demonstration that eV surpasses the absorption threshold at room temperature under illumination conditions similar to 0.5 suns.

Finally, in order to increase the research capabilities of the IES-UPM, we implemented during this Thesis an experimental set-up dedicated to the “Deep-Level Transient Spectroscopy” (DLTS) technique. This technique provides information about

recombination processes and complements the characterization obtained from optical techniques, focused on studying electron-hole pairs generation processes.

Symbol List

α_{XY}	cm^{-1}	Absorption coefficient for transitions from band X to band Y
ε	$\text{F} \cdot \text{cm}^{-1}$	Dielectric constant
ε_0	$\text{F} \cdot \text{cm}^{-1}$	Vacuum permittivity
$\mathcal{E}_0$	$\text{V} \cdot \text{cm}$	Surface electric field
Δ	eV	Intermediate band width
ΔG	eV	Variation of the Gibbs free energy
ΔH	eV	Variation of the enthalpy
ΔS	$\text{eV} \cdot \text{K}^{-1}$	Variation of the entropy
ΔV	eV	Band-offset between a host material and a quantum dot
ε_{Fe}	eV	Quasi-Fermi level of electrons at the conduction band
ε_{Fh}	eV	Quasi-Fermi level of holes at the valence band
ε_{FIB}	eV	Quasi-Fermi level of carriers at the intermediate band
η	-	Solar cell efficiency
θ_s	rad	Maximum angle of a ray bundle coming from the Sun
μ	eV	Electrochemical potential
μ_{XY}	eV	Split between the quasi-Fermi levels associated to band X and band Y
v_{th}	$\text{cm} \cdot \text{s}^{-1}$	Carrier thermal velocity
ρ	$\text{C} \cdot \text{cm}^{-3}$	Charge density
σ_n	cm^2	Electron capture cross section
σ_p	cm^2	Hole capture cross section
ϕ	V	Electrostatic potential
A	cm^2	Device area

C	F	Capacitance
C_{M0}	eV	Coupling parameter used in the band-anticrossing model
C_P	F	Parallel capacitance
C_S	F	Series capacitance
$c_n n$	s^{-1}	Electron capture rate
$c_p p$	s^{-1}	Hole capture rate
E_G	eV	Fundamental bandgap (between the valence band and the conduction band)
E_H	eV	The highest gap delimited by the intermediate band (usually, between the valence band and the intermediate band)
E_i^0	eV	Intrinsic level
E_{IB}^0	eV	Energy of the intermediate band
E_L	eV	The narrowest gap delimited by the intermediate band (usually, between the intermediate band and the conduction band)
e	C	Electron charge
e_n	s^{-1}	Electron emission rate
e_p	s^{-1}	Hole emission rate
G	S	Conductance
h	eV · s	Plank's constant
J	$A \cdot cm^{-2}$	Current density
J_0	$A \cdot cm^{-2}$	Inverse saturation current density
J_{Di}	$A \cdot cm^{-2}$	Dark current density of a diode D_i
j_{Di}	$A \cdot cm^{-2}$	Small signal dark current density of a diode D_i
J_e	$A \cdot cm^{-2}$	Electron current density
J_h	$A \cdot cm^{-2}$	Hole current density

J_L	$A \cdot cm^{-2}$	Photogenerated-current density
J_{ph}	$A \cdot cm^{-2}$	Photogenerated-current density under monochromatic illumination
j_{ph}	$A \cdot cm^{-2}$	Small-signal photogenerated-current density under monochromatic illumination
J_{SC}	$A \cdot cm^{-2}$	Short-circuit current density
k_B	$eV \cdot K^{-1}$	Boltzmann's constant
L	nm	Length of a quantum box
m	-	Ideality factor of a p-n junction
m^*	kg	Carrier effective mass
$\dot{N}$	$cm^{-3} \cdot s^{-1}$	Number of photons emitted per unit time and per unit area
n	cm^{-3}	Electron concentration in the conduction band
N_A	cm^{-3}	Acceptor doping density
N_{AIB}	cm^{-3}	Acceptor-states that form the intermediate band per unit of volume
N_C	cm^{-3}	Effective density of the energy states in the conduction band
N_D	cm^{-3}	Donor doping density
N_{DIB}	cm^{-3}	Donor-states that form the intermediate band per unit of volume
N_I	cm^{-3}	Energy states that form the intermediate band per unit of volume
N_{SCR}	cm^{-3}	Charge density of the space charge region divided by the electron charge
N_T	cm^{-3}	Trap density
n_I	cm^{-3}	Electron concentration in the intermediate band
n_i	cm^{-3}	Intrinsic carrier concentration
n_T	cm^{-3}	Concentration of donor-traps occupied by electrons

p	cm^{-3}	Hole concentration in the valence band
p_I	cm^{-3}	Hole concentration in the intermediate band
p_T	cm^{-3}	Concentration of acceptor-traps occupied by holes
Q_{IB}	$\text{C} \cdot \text{cm}^{-3}$	Charge density associated to the intermediate band
R_S	$\Omega \cdot \text{cm}^2$	Series resistance
r_i	$\Omega \cdot \text{cm}^2$	Small-signal diode resistance
T	K	Temperature
t	s	Time
V	V	Voltage
V_{bi}	V	Built-in voltage
V_f	V	Forward voltage
V_{OC}	V	Open-circuit voltage
V_r	V	Reverse voltage
WR	s^{-1}	Window rate
X	-	Concentration factor
x_{SCR}	nm	Width of the space charge region

Acronym List

2JSC	Double junction tandem solar cell
BAC	Band-anticrossing
CB	Conduction band
cw	Continuous-wave
CV	Capacitance-voltage
DL	Deep level
DLTS	Deep level transient spectroscopy
EL	Electroluminescence
EQE	External quantum efficiency
ES	Excite state
FDL	Field damping layer
FF	Fill factor
HMA	Highly mismatch alloy
IB	Intermediate band
IBSC	Intermediate band solar cell
IR	Infra-red
MBE	Molecular beam epitaxy
MJSC	Multi-junction solar cell
MPE	Multi-phonon emission
NOV	Not overlap
NRR	Non-radiative recombination
OV	Overlap
PECVD	Plasma-enhanced chemical vapor deposition

PL	Photo-luminescence
PLM	Pulsed laser melting
PR	Photo-reflectance
PV	Photovoltaic
QD	Quantum dot
QW	Quantum well
QWr	Quantum wire
RT	Room temperature
SCR	Space charge region
SQ	Shockley-Queisser
SR	Spectral response
SRH	Shockley-Read-Hall
UCM	Universidad Complutense de Madrid
UPC	Universidad Polit�cnica de Catalu�a
VB	Valence band
VBO	Valence band offset
WL	Wetting layer

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1 INTRODUCTION

Photovoltaic (PV) solar energy is one of the most promising energy sources. Its main advantage relies on exploiting an inexhaustible source, the sun. Besides, this resource is widely distributed and provides enough energy to satisfy the current demand of energetic consumption. An idea of the value of these magnitudes is inferred from the fact that the amount of sunlight energy that can flow through an area of $15,000 \text{ km}^2$ each second is roughly equal to the average power demand of the whole of humanity, which is around 15 TW [Dale'13]. Some years ago, the low development level of the PV technology impeded this energy source to be as competitive as others, such as natural gas or wind power. However, nowadays, the continuous fall of the levelized cost of electricity (LCOE) of PV technology as well as the increasing costs of some other technologies, such as fossil fuel power plants, leads to a constantly improving competitive position for the PV technology in some regions such as Germany [Kost'13]. In order for PV technology to reach price parity with conventional electricity sources, different research directions can be followed. These directions are on how to reduce the module manufacturing cost, on how to reduce the degradation rate, on how to increase the service lifetime and finally on how to increase the efficiency. These parameters impact the 2015 baseline LCOE in different ways, which is analyzed in detail in [Jones-Albertus'15].

Increasing the conversion efficiency is a good strategy because it significantly reduces the “balance of system” cost (all costs except the PV module), which account for about one half of the installed cost of a commercial or utility PV system [Bony'10]. To increase the efficiency of solar cells, alternatives to conventional single gap solar cells have been developed. These new solar cell are sometimes known as “third generation solar cells” and are defined as not being subjected to the Shockley-Queisser (SQ) efficiency limit,

which is of 40.7% under black body radiation and maximum concentration [Shockley'61]. The efficiency of third generation solar cells increases in respect to conventional single gap solar cells because the transmission and the thermal losses are reduced in them. Transmission losses are due to non-absorption of photons with energy below the bandgap. Thermal losses are produced because carriers generated by photon energies higher than the bandgap relax to the bandgap edge. In order to reduce these energetic losses different families of solar cells have been researched. Some of them have reached a mature stage, such as multi-junction solar cells (MJSCs), and others are in development stages, such as hot carrier solar cells, multiple exciton generation solar cells and intermediate band solar cells (IBSCs).

This Thesis aims to contribute to the research in the field of IBSCs, characterized by a limiting efficiency of 63.2% under maximum concentrated light due to the presence of an intermediate band (IB) that makes it possible for additional optical transitions below the bandgap to occur [Luque'97b]. The first and most studied way to implement this IB has been based on the introduction of quantum dot stacked layers [Martí'00]. This approach has provided encouraging results [Wagener'14]. However, theoretical and experimental works have revealed that, in this kind of systems, the optical transitions through the IB are characterized by low absorption coefficients [Antolin'10; Mellor'14]. For this reason, another line of research has been proposed: manufacturing IB materials based on the introduction of suitable impurity atoms in a host material [Luque'06a]. Some research groups, such as groups from the Lawrence Berkeley Laboratory, the University of Michigan and the Universidad Complutense de Madrid, aim to develop this family of materials but, so far, they still remain the least investigated ones.

In this Thesis, our work has been devoted to study some of these material systems in collaboration with some of the above mentioned research groups. Several optoelectronic techniques, such as spectral response and current-voltage measurements, have been used to characterize these samples and demonstrate the operation principles of the IBSC. Also, a study in depth about the application of capacitive techniques on IBSCs has been carried out, for the first time, in this Thesis. This has required the development of an experimental set-up dedicated for the "Deep Level Transient Spectroscopy" (DLTS) technique.

1.1 The intermediate band solar cell (IBSC)

1.1.1 Operation principles of the IBSC

The concept of IBSC was presented in 1997 by A. Luque and A. Martí [Luque'97b]. One of the reasons why the limiting efficiency of this device surpasses the SQ limit is because the presence of energy levels inside the bandgap allows sub-bandgap energy photons to be absorbed. The idea of taking advantage of energy levels present inside the semiconductor bandgap was also postulated in an early work by Wolf [Wolf'60]. In that work, these energy levels were used by devices called multi-transition solar cells to yield conversion efficiencies higher than those of single p-n junction devices. However, multi-transition solar cells were tested [Grimmeiss'61] and it was concluded that these devices could increase the photocurrent, but not the efficiency. The reason was that voltage was not preserved in multi-transition solar cells. However, this limitation is avoided in IBSCs.

In single gap solar cells, an increase in photocurrent can be achieved by reducing the bandgap. However this would imply also a reduction of the output voltage¹, because the value of this voltage is limited by the bandgap of the semiconductor. This fact is illustrated by means of Fig. 1.1, where the ideal current density-voltage characteristics for conventional solar cells with different bandgaps (E_G) evidence that, a low bandgap results in a high short-circuit current density (J_{SC}) and a low open-circuit voltage (V_{OC}), and a high bandgap results in a low J_{SC} and a high V_{OC} . The efficiency of the IBSC surpasses the SQ limit because this device breaks this trade-off between current and voltage. In these solar cells the photocurrent can be increased without reducing the voltage. To understand how this is possible, it is necessary to fathom the physical principles governing the IBSC operation. We will explain this, step by step, starting with the description of the general structure on an IBSC.

¹To prevent photon stimulated emission overcoming absorption processes in single gap solar cells, the electron and hole quasi-Fermi levels split cannot be higher than the bandgap of the semiconductor [Casey'78]. In conventional solar cells this split is proportional to the output voltage, so that the output voltage is limited by the bandgap value divided by the electron charge.

Fig. 1.1: Ideal current density – voltage characteristic under maximum sunlight concentration ($X=46050$). The current density is expressed as current per unit of concentrator area. The black curve corresponds to the characteristic of an optimal IBSC. It is compared with the characteristic of a single gap solar cell with low bandgap ($E_G = 0.71\text{eV}$, red curve) and a single gap solar cell with high bandgap ($E_G = 1.95\text{eV}$, blue curve). The legend manifests that the ideal efficiency of an optimal IBSC ($\eta = 63.2\%$) surpasses the SQ limit efficiency for single gap solar cells ($\eta = 40.7\%$).

As depicted in Fig. 1.2, an IBSC is based on an absorbing material (the IB material) separated from the metal contacts by means of conventional p-type and n-type semiconductors (also called selective contacts or emitters). In the IB material there are three energy bands, the valence band (VB), the IB and the conduction band (CB). Three different quasi-Fermi levels can be defined to describe the electronic population in each band, ε_{Fh} , ε_{FIB} and ε_{Fe} respectively. This arrangement splits the total bandgap of the IB semiconductor, E_G , in two sub-bandgaps, E_L (for the lowest sub-bandgap) and E_H (for the highest sub-bandgap) and therefore, it allows additional electronic processes to take place (Fig. 1.2), to know: generation processes between the VB and the IB (g_{VI}), the IB and the CB (g_{IC}), and recombination processes between these same bands (r_{VI} and r_{IC} respectively). In an IBSC the position of the quasi-Fermi levels depends on the electronic population of the corresponding energy band. These electronic populations are affected by the electronic processes of generation, recombination and by carrier transport. The intensity of these processes depends on the operation conditions so that: (1) under equilibrium, the three quasi-Fermi levels are equal because generation processes and recombination processes compensate and net transport is not produced; (2) under normal solar cell operating conditions (illumination and forward bias below V_{OC}) generation processes dominate recombination process and net transport is produced. Because carriers in each band are not in equilibrium, split of quasi-Fermi levels is produced.

Fig. 1.2: Structure of IBSCs (top) and corresponding band diagram under equilibrium (middle) and operating conditions (bottom). Under equilibrium, processes g_{VI} , g_{IC} and g_{VC} are related with thermal generation and are compensated with recombination processes so that $g_{VI} = r_{VI}$, $g_{IC} = r_{IC}$ and $g_{VC} = r_{VC}$. The generation processes are intensified by optical transitions under operating conditions.

The rate of the generation and recombination electronic transitions can be described by the Shockley-Read-Hall (SRH) model [Hall'52; Shockley'52], which can be used regardless of the physical mechanism behind these generation-recombination processes [Luque'10b; Martí'04]. Traditionally, the energy levels within the semiconductor bandgap have been considered a source of non-radiative recombination that degrades the

performance of the solar cells when these levels are located close to the mid-gap. From this perspective this kind of energy levels are undesirable. However, the IBSC theory considers that the recombination processes to and from these energy levels are dominantly of radiative nature. From this other perspective, the presence of an IB can enhance the performance of a solar cell if the power gain due the increase in photocurrent compensates the power loss due to the increase in recombination.

In an IBSC, electrons can be generated in the CB, holes can be generated in the VB and both carriers can be generated in the IB. The selective contacts used in this device imply that only electrons from the CB and holes from the VB can be extracted into the external circuit with electrochemical potentials equal to ε_{Fe} and ε_{Fh} respectively. So, the output voltage multiplied by the electron charge is the difference between ε_{Fe} and ε_{Fh} , which is limited by E_{G} , as in conventional solar cells. This operation principle is general for all single gap solar cells, and it is known as “voltage preservation principle” in the context of IBSCs. According to the IBSC theory, in these devices the extracted carriers can be generated by the two kinds of processes indicated in Fig. 1.3: (a) the absorption of one photon whose energy is higher than E_{G} (labelled as 3), and (b) the absorption of two sub-bandgap photons whose energies are higher than E_{H} (labelled 2) and E_{L} (labelled 1). The latter process leads to what is commonly known as “two-photon sub-bandgap photocurrent” and it is the other operation principle the IBSC is based on. These two operation principles imply that IBSCs can supply voltages as high as the ones of single gap solar cells with bandgap E_{G} and photocurrents as high as the ones of single gap solar cells with bandgap lower than E_{G} . This is why the IBSC breaks the trade-off between current and voltage of conventional solar cells.

Fig. 1.3: Band diagram of an IBSC showing the mechanisms that produce the output power behind the operation of an IBSC. J is formed by the electrons extracted from CB and holes extracted from VB, generated by the absorption of supra-bandgap photons (3) and the absorption of sub-bandgap photons (1 and 2). V is

determined by $(\varepsilon_{Fe} - \varepsilon_{Fh})/e$.

To facilitate the comprehension of how IBSCs operate, it may be useful to illustrate also the operation of an IBSC in terms of its equivalent electric circuit [Luque'04]. This circuit is illustrated in Fig. 1.4. In this ideal circuit (series resistance, parallel resistance and absorption coefficient overlap are neglected), the current density generators represent the optical transitions associated to the generation of carriers (which are labeled as 1, 2 and 3 in accordance with Fig. 1.3) and the diodes represent the radiative recombination processes. This scheme lets us visualizing the IBSC as the result of connecting one solar cell with a bandgap E_G in parallel with two solar cells with bandgaps E_H and E_L , which are connected in series. This series connection implies J_L is equal to J_H . A necessary condition for these current densities to contribute to the extracted J is that the IB must neither be full of electrons to allow transitions $VB \rightarrow IB$ to take place (J_{LH}) nor empty of electrons to allow transitions $IB \rightarrow CB$ (J_{LL}). This condition is analyzed in more detail in Section 1.1.3.

Fig. 1.4: Equivalent circuit of an ideal IBSC. The current density generators represent the optical transitions associated to the generation of carriers and the diodes represent the radiative recombination processes.

1.1.2 Limiting efficiency of the IBSC

Once we understand the advantages offered by IBSCs, it is important to study to what extent we can exploit this new concept. To this end we use the detail balance model. This model determine the thermodynamic efficiency limit of solar cells assuming that in these devices there is only one path for recombine carriers, the unavoidable radiative recombination processes [Shockley'61]. This model is used in [Luque'97b] to obtain the current-voltage ($J - V$) characteristic of IBSCs. In that work, J is obtained analyzing the

flux of photons absorbed by the solar cell and the flux of photons emitted by the solar cell. These fluxes are obtained by Plank's law, which gives the number of photons emitted, $\dot{N}$, with energies between E_1 and E_2 per unit time and per unit area of emitting surface ($\text{photons} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$), whose temperature is T and electrochemical potential is μ . Assuming that surfaces have an emissivity equal to 1, then:

$$\dot{N}(E_1, E_2, \mu, T) = \frac{\pi}{h^3 c^2} \int_{E_1}^{E_2} \frac{E^2}{\exp\left(\frac{E - \mu}{k_B T}\right) - 1} dE \quad (1.1)$$

For the photons generated in semiconductors, the electrochemical potential equals the difference between the quasi-Fermi levels of the energy bands involved in the electric transition.

$$\begin{aligned} \mu_{CV} &= \varepsilon_{Fe} - \varepsilon_{Fh} \\ \mu_{CI} &= \varepsilon_{Fe} - \varepsilon_{FIB} \\ \mu_{IV} &= \varepsilon_{FIB} - \varepsilon_{Fh} \end{aligned} \quad (1.2)$$

Assuming that ε_{Fh} , ε_{FIB} and ε_{Fe} are constant through the solar cell, it is possible to relate these quasi-Fermi levels with V .

$$\mu_{CV} = \mu_{CI} - \mu_{IV} = eV \quad (1.3)$$

It is important to point out that this assumption implies that the mobility of electrons in the CB and holes in the VB approach infinite. Carriers in the IB do not need to have infinite mobility because the current density extracted from the IB is zero [Martí'12].

Another assumption consists of considering that the sun and the surroundings of the solar cells are black bodies at temperatures T_S and T_E respectively, and the IBSC a body at T_C . Under these circumstances J can be calculated by:

$$\begin{aligned} J = J_e &= e \{ X(\sin\theta_S)^2 [\dot{N}(E_L, E_H, 0, T_S) + \dot{N}(E_G, \infty, 0, T_S)] \\ &\quad + [1 - X(\sin\theta_S)^2] [\dot{N}(E_L, E_H, 0, T_E) + \dot{N}(E_G, \infty, 0, T_E)] \\ &\quad - [\dot{N}(E_L, E_H, \mu_{CI}, T_C) + \dot{N}(E_G, \infty, \mu_{CI}, T_C)] \} \end{aligned} \quad (1.4)$$

$$\begin{aligned} J = J_h &= e \{ X(\sin\theta_S)^2 [\dot{N}(E_H, E_G, 0, T_S) + \dot{N}(E_G, \infty, 0, T_S)] \\ &\quad + [1 - X(\sin\theta_S)^2] [\dot{N}(E_H, E_G, 0, T_E) + \dot{N}(E_G, \infty, 0, T_E)] \\ &\quad - [\dot{N}(E_H, E_G, \mu_{IV}, T_C) + \dot{N}(E_G, \infty, \mu_{IV}, T_C)] \} \end{aligned} \quad (1.5)$$

These equations give the dependence of the current density of the electrons in CB (J_e) and the current density of the holes in VB (J_h) with V . In these equations e is the electron charge, θ_S is the subtended angle of the Sun, and X is the sunlight geometrical concentration.

The limiting efficiency of the IBSCs is obtained by solving these equations and finding the point of maximum power of the $J - V$ characteristic. This limiting efficiency is plotted in Fig. 1.5 as a function of the lowest bandgap while the largest is optimized assuming maximum sunlight concentration (46050 suns). Several assumptions have been made to obtain these results: (1) All intermediate levels have the same energy, which means that IB is an energy band of zero width; (2) All photons with energy higher than E_L are absorbed; (3) Photons of a given energy can only be absorbed in one optical transition, in the most energetic possible one; (4) Photons emitted by the solar cell can be reabsorbed by means of photon recycling; (5) A perfect mirror is located at the back of the solar cell. These assumptions and the calculations are detailed in [Luque'97b].

Fig. 1.5: Detailed balance efficiency limit of IBSCs compared to that of a double-junction tandem solar cell and a single gap solar cell. The efficiency is plotted as function of the lowest bandgap involved in each structure. In the case of the IBSC the lowest bandgap is E_L (denoted as ε_l in the figure). If appropriate, the corresponding value of the highest bandgap involved in each structure is indicated (after [Luque'97b]).

Fig. 1.5 compares the limiting efficiency of single gap solar cells, double junction tandem solar cells and IBSCs. This comparison evidences the superior potential of the IBSC, which can reach a limiting efficiency of 63.2% for the optimal bandgap distribution given by $E_G = 1.95$ eV, $E_L = 0.71$ eV and $E_H = 1.24$ eV. This efficiency can be increased by using selective energy reflector filters [Strandberg'10] or tandems of two or more IBSCs [Antolín'06].

1.1.3 Intermediate band (IB) properties

It is important to emphasize that an ideal IB is a grouping of energy states that guarantee both: (1) the absorption of each photon of the solar spectrum with energies $E_H \leq E < E_G$ and $E_L \leq E < E_H$ through the generation processes g_{VI} and g_{IC} respectively, and (2) the radiative nature of the recombination processes r_{VI} and r_{IC} .

A necessary condition to fulfill requirement (1) is that the IB is partially filled, which is to say, ε_{FIB} is located inside the IB. There are several ways to achieve this condition. For example, this could be reached, in steady state conditions, by illuminating the IBSC and photo-filling with carriers the intermediate levels. However, a high light concentration level would be required in order to approximate the efficiency limits of Fig. 1.5 [Luque'10b; Strandberg'09]. Another option could be engineering the IBSC so that the IB would be partially filled naturally at room temperature. Finally, the last option would consist in doping the intermediate levels, which would ensure the partial filling in equilibrium conditions. In order to ensure also this partial filling under operation conditions, the density of IB-states should be higher than the variation of the concentration of electrons and holes in the IB. These variations depend on the light intensity, output voltage, absorption coefficients and capture cross sections. Therefore, different density of IB-states are demanded depending on the operating conditions and the value of these parameters [Marti'12].

The presence of an IB makes three generation processes possible, g_{VC} , g_{VI} and g_{IC} . The probability of these processes occurring is described respectively by three absorption coefficients, α_{VC} , α_{VI} and α_{IC} . In order to guarantee requirement (1), the qualitative dependence of these coefficients with the photon energy should be that shown in Fig. 1.6. The absorption coefficients that follow these dependences are known as selective absorption coefficients or non-overlapped absorption coefficients. The reason is because, for each photon energy value, only one absorption coefficient can be non-zero. For a given photon energy, the non-zero absorption coefficient is the one related with the highest energetic transition possible at that photon energy. The impact of the selective character of absorption coefficients in the efficiency of IBSCs was studied in [Cuadra'04b], and will be revisited in Section 3.2.

Fig. 1.6: (left) Representation of the three generation processes that can take place in IBSCs, g_{VC} , g_{VI} and g_{IC} . The intensity of these processes depends on the absorption coefficients α_{VC} , α_{VI} and α_{IC} respectively. On the right side, the dependence of these coefficients with the photon energies is plotted for the case of an ideal IBSC. Note that this is a qualitative representation which only tries to emphasize the selective character of the absorption coefficients.

In order to fulfill requirement (2), it is recommendable that the intermediate energy levels are de-localized [Luque'06a] which is one of the reasons why we call this collection of intermediate levels “band”. Depending on the implementation of the IB, delocalized energy levels means that their wave function extends over all the crystal lattice or their wave function extends over several atoms [Martí'13]. This will be seen Sections 1.2.1 and 1.2.2.

Another feature of the IB is its bandwidth. In Section 1.1.2, a zero bandwidth IB was considered in order to obtain the limiting efficiencies in Fig. 1.5. This assumption implies that the mobility of the IB-carriers is zero, since a zero bandwidth is associated to an infinite effective mass [Yu'10]. In spite of IB-carriers with zero mobility not impeding the IBSC operating principles [Martí'12], high mobility for carriers in the IB can be recommendable in order to homogenize the electron and hole generation when the IBSC is illuminated [Martí'02]. To this end, an IB with a bandwidth, Δ , different to zero, would be required. This case was studied in [Cuadra'00], where the IB bandwidth is described by $\Delta = E_{IH} - E_{IL}$, defining E_{IL} and E_{IH} as the lower and higher energy level of the IB respectively. The analysis carried out in that work revealed that, for an appropriate operation, the IB bandwidth needs to be limited by an upper bound. This restriction has its origin in the necessity to prevent the photon stimulated emission overcoming the absorption processes. This condition requires that μ_{IV} does not exceed E_H and μ_{CI} does not exceed E_L , and therefore, implies that the bandwidth of an IB must fulfill:

$$eV = \mu_{IV} + \mu_{CI} < E_{CL} - E_{IH} + E_{IL} - E_{VH} = E_G - \Delta \quad (1.9)$$

In this equation E_{VH} and E_{CL} are the upper energy level of the VB and the lower energy level of the CB respectively. Equation (1.9) reveals that Δ needs to be limited. For example, should the maximum sunlight concentration be used to illuminate an IBSC, then Δ must be ≤ 177 meV at the maximum power point, while $\Delta \leq 744$ meV for operation at

one sun illumination [Cuadra'00]. The mobility of electrons and holes in the IB will depend on the bandwidth, Δ [Martí'12].

1.2 IB material implementations

To our knowledge, no conventional semiconductor behaves as an IB material. This makes the fabrication of IB materials a technological challenge for which new materials need to be engineered. To this end, different technologies are under investigation. They can be divided into two large groups: nanostructures, such as quantum dots [Martí'00], and semiconductor bulk materials formed by highly mismatched alloys [Shan'99] or containing a high density of deep-level impurities [Luque'06a]. In addition, other interesting configurations have been proposed, as for example the molecular approach [Ekins-Daukes'08] which are outside the scope of this Thesis.

1.2.1 The nanostructure technology

In semiconductor electronics, the term nanostructure refers to very small semiconductor crystals, typically of nano-metric scale. When a nanostructure is embedded in a different semiconductor material (called host material), the alignment of the energy bands can generate the appearance of electron confinement potentials in the CB and the VB (Fig. 1.7). Electrons confined in these potentials have a specific energy, which can be calculated by solving the Schrödinger equation for the Hamiltonian that describes the system [Luque'11b]. In the simplest case, in which the problem is unidimensional and the shape of the potential is a rectangular box, as depicted in Fig. 1.7, with a width L and an infinite band-offset between the host material (also called barrier material) and the QD ($\Delta V = \infty$), the energy of the confined states is given by [Harrison'06]:

$$E_i = \frac{\hbar^2 \pi^2}{2m^*} \cdot \frac{n_i^2}{L^2} \quad (1.10)$$

where $\hbar$ is the reduced Planck constant, m^* is the carrier effective mass and n_i is the quantum number (1,2,3...).

Fig. 1.7: Band diagram of a potential pedestal in the VB (left) and a potential well in the CB (right). The shape and the size of these potentials (L and ΔV), and the energy of the confined states (E_i) are indicated. If these states have an energy higher than ΔV (they are situated within the VB and CB), they are called virtual bound states [Luque'13].

In practice, the band-offset between barrier and dot is finite ($\Delta V < \infty$) and a similar tendency to that shown by equation (1.10) is obtained, so that E_i increases if L decreases, m^* decreases or ΔV increases.

Three different nanostructures can be defined depending on the number of dimensions in which electrons are confined: quantum wells (QWs), quantum wires (QWr) and quantum dots (QDs). In QWs electrons are confined in one-dimension. In QWr electrons are confined in two-dimensions. Finally, QDs are the nanostructures in which the electrons are confined in three-dimensions. This three-dimensional confinement makes QD the only nanostructure that can exhibit a true zero density of states between the confinement states and the bandgap of the host semiconductor [Weisbuch'91]. For this reason, QDs were proposed in [Martí'00] as one of the approaches used to implement IB materials. The wave function of the electrons confined in these states extends over several atoms, therefore, these states can be considered as de-localized [Martí'13].

QD-IBSC prototypes have shown some practical drawbacks. One of them is the presence of strong thermal generation² and recombination processes. The intensity of these processes is increased by the presence of excited states as those labelled ES_1 and ES_2 in Fig. 1.8 [Antolin'10]. Ideal material combinations would lead to ground states (labelled GS in Fig. 1.8) with energies delimited between the minimum of the CB and the maximum of the VB, and excited states with energies outside of this range. The election of suitable material combinations can reduce thermal processes and also solve other inconveniences, such as the VB offset (VBO) produced in type-I QDs. This VBO reduces the output voltage

²In principle, thermal generation is not harmful to solar cells because it neither impairs nor improves the performance. However, thermal generation is an undesirable process because its presence implies the presence of the undesired thermal recombination.

and it can be solved by using type-II QDs in which the VB alignment does not produce a potential pedestal. Other problems evidenced in practice by QD-IBSC prototypes are related to the techniques used to fabricate these devices. The epitaxial techniques, commonly used to fabricate QDs, have usually used the Stranski- Krastanov (SK) mode in which QDs are formed due to the strain produced by the difference in lattice constant between the QD semiconductor and the barrier semiconductor [Krastanow'38]. In this technique, at least the QDs of the first layer nucleate spontaneously without control over its individual positioning. The shape, size and composition of each QD cannot be completely controlled, which can lead to non-homogeneities in the band diagram. Besides, techniques based on SK usually lead to the formation of a very thin layer (0.5–3 nm) called wetting layer (WL), underneath the QD layer forming a QW structure (as depicted in Fig. 1.8). This WL also contributes to the reduction of the output voltage and it may be avoided by using other growth techniques such as techniques where QDs are formed by the difference in crystal structure between the QD and the barrier material [Antolin'11].

Fig. 1.8 shows the band diagram of type-I QDs grown with the SK mode, which will be the only ones studied in this Thesis. The above mentioned drawbacks are illustrated in the figure.

Fig. 1.8: Typical band diagram of two type-I QDs grown by the SK mode with two different sizes (the smallest on the right, the largest on the left). The VBO, the confined states (GS, ES₁ and ES₂) and the corresponding bandgaps E_L , E_H and E_G are indicated. Note that, in spite of the fact that the QD and the WL are made of the same material, the energy level distribution of these nanostructures is different. The value of E_{QD} can be different to the bandgap of the bulk material that forms the QDs and the WLs due to the strain resulting from the lattice difference between dot and barrier material.

In addition to the above mentioned drawbacks, maybe the most important inconvenience of QDs is the weak absorption in the optical transitions that involve the QD electronic states. The main reasons for this are the low volumetric QD density (in the

$10^{15} - 10^{16} \text{cm}^{-3}$ range) and the limited number of the QD layers that can be stacked (typically less than 50) during the growth because of the accumulation of strain or time of growth needed. On one hand, the QD volumetric density can be increased by, for example, using substrates with higher crystallographic index [Aka 98, Aka 02] and/or by reducing the thickness of the barriers between QD layers. On the other hand, the number of QD-layers that can be grown with good optoelectronic properties can be increased by reducing the accumulated strain [Oshima'08; Popescu'08; Wei-Sheng'12]. Another strategy to increase the absorption in the optical transitions that involve the QD electronic states consists in reducing the QD size. According to [Mellor'12; Mellor'13], this size reduction can increase the strength of the optical transitions between QD states. However, variations in the QD size lead to different positioning of the energy levels, which needs to be taken into account. A compromise must be made between increasing the strength of these transitions and obtaining an optimum level distribution to determine the optimum QD size that maximizes the sub-bandgap photocurrent in each material system.

1.2.2 The bulk approach

Another approach to implement IB materials consists of the fabrication of semiconductor materials that contain a high density of impurities introducing a suitable deep level in the semiconductor bandgap [Luque'06a] and the fabrication of highly mismatched alloys (HMAs) [Shan'99]. A common characteristic of these two material families is that both are the result of introducing atoms of a foreign specie inside the lattice of a host semiconductor. We will refer to these atoms as impurities. The difference between these two material families is the result of the impurity-host interaction.

The result of the impurity-host interaction may be the emergence of discrete levels inside the bandgap of the semiconductor. In this case, an IB can be formed from these energy levels if they are situated at a significant distance from the VB and CB, receiving the name of “deep-levels” (DLs) (Fig. 1.9b). The wave function of DLs is usually localized at the impurities position, unlike the de-localized wave function of states in the CB and the VB. The overlap between localized and de-localized wave functions is small, which reduces the probability of optical transitions taking place between the states in the CB and DLs, and between DLs and states in the VB [Loudon'64]. This is why, for the DLs present in conventional semiconductors, the rate of radiative recombination is usually lower than the rate of non-radiative recombination (NRR) [Queisser'78]. In order to form an IB from DLs, it is necessary to inhibit the NRR associated with these levels. One way to reach this is by delocalizing the wave function of DLs. This was proposed for the first time in [Luque'06a], where it was predicted that the inhibition of NRR requires increasing the amount of impurities beyond a specific value. We will refer to this value as the Luque limit. According to [Luque'06a], increasing the amount of impurities until the Luque limit is exceeded

allows an IB to be formed. The inhibition of the NRR by increasing the amount of impurities is one of the physical principles of DLs-IBSC. Krich *et al.* have argued against this principle because, according to their predictions, the metallic extended states will be localized by phonons during the recombination process [Krich'12]. The NRR suppression will be studied in Section 3.1.

On the other hand, in some HMAs, the impurity-host interaction perturbs the CB states and splits this energy band into E_+ and E_- . This phenomenon is known as band anti-crossing mechanism and it is produced when highly electronegative atoms are introduced into a binary host material in a fraction in the order of 1-5 % [Shan'99; Walukiewicz'00]. In these materials the IB can be formed from the lower energetic band, E_- , as depicted in Fig. 1.9(c).

Fig. 1.9: (Top) Sketch of the physical implementation of IB materials according to the bulk approach. (Bottom) Simplification of the band diagram resulting from the use of DLs (a) and HMAs (b).

One of the major difficulties to implement these material families consists of finding which combinations of host semiconductors and impurities lead to the formation of an optimum band diagram. In an optimum band diagram distribution, the IB should be located at 0.71 eV from one of the energy bands of the host semiconductor, which should have a bandgap of 1.95 eV [Luque'97b]). Several works have been devoted to this aim, providing several possible material combinations [Wahnon'02]. For these material systems the Luque limit usually exceeds the solubility limit of the impurity in the semiconductor. This makes the incorporation of impurities at a concentration greater than the Luque limit a technological challenge. In some cases, this solubility limit can be overcome via low-temperature epitaxial growth [Campion'03]. In other cases, non-equilibrium methods are used, such as ionic implantation combined with rapid thermal laser annealing [Castán'13; Persans'12]. These procedures have no control over the

position of atoms and they usually lead to the emergence of crystalline defects that degrade the electro-optical properties of the semiconductors.

Although the bulk approach presents these difficulties, it can offer some advantages with respect to the approach based on QDs. In particular, since impurity densities can be rather higher than QD densities, a higher density of states could be present in an IB formed from DLs or HMAs than in an IB formed from QDs. From this perspective, it could be assumed that the bulk approach can lead to volumetric absorption coefficients higher than the volumetric absorption coefficients resulting from the QD approach, because more photons can be absorbed in the first case. However, this is not clear because the probability of absorption processes depends strongly on the optical cross section, which may be higher in the case of QDs as a consequence of their higher size with respect to the size of the impurities. This discussion is detailed in [Luque'10a], where it is concluded that IB materials based on the bulk approach can have better optical properties.

1.3 State of the art of IBSCs

The general aim of an IBSC is to provide a higher efficiency than the efficiency of its corresponding reference solar cell, without IB. In order to progress towards this goal, to date, research has been focused on demonstrating the IBSC operating principles mentioned in Section 1.1.1. These operating principles are: (1) the generation of two-photon sub-bandgap photocurrent and (2) the achievement of an output voltage with no limitation from the IB. This Section summarizes the advances in IBSC research obtained from 1997 to September 2015 (which are reviewed in detail in [Ramiro'14b]), with the exception of the results presented in the following Chapters of this Thesis.

IBSCs prototypes based on InAs/GaAs³ QDs were the first candidates studied because of the technological maturity of this material system. Within and outside the IBSC context, the presence of sub-bandgap transitions was evidenced in this material system by means of photoluminescence [Phillips'97], electroluminescence [Luque'05;Ramiro'11], absorption [Durr'98;Sauvage'97;Xu'98] and photo-reflectance measurements [Cánovas'08;Marron'13;Sun'98]. Some years after the IBSC concept was revealed (1997), spectral response measurements evidenced the production of photocurrent through sub-bandgap transitions in this material system [Luque'04]. However, it was not until 2006 when it was possible to demonstrate that the sub-bandgap photocurrent could be

³In this Thesis, when referring to a QD system, we will use the notation X/Y, where X is the QD material and Y is the barrier material or the material of the host semiconductor.

produced by a two-photon effect [Martí'06a], which is one of the two key principles of IBSCs. Reducing the temperature of the solar cell to 36 K was required to demonstrate this principle. Cryogenic temperature also had to be used in [Antolín'10] to prove that the voltage of the cell was not limited by the IB, which is the other operating principle of IBSCs. In order to improve these results, some practical problems of this material system were attended. Some examples are cited below. A better distribution of the bandgaps was obtained by covering the QD layers with "strain relief layers" based on quaternary alloys in [Antolín'10]. In the same work, the inclusion of a small amount of N, P or Sb in the host material reduced the accumulated strain in the QD-stack and improved the material quality. The same was obtained by increasing the width of the barrier layers of the QDs in [Martí'07]. In spite of all the improvements, the advances in InAs/GaAs QD-IBSC prototypes were always limited by the fact that the bandgap of the GaAs barriers (~ 1.42 eV) is too low when compared to the optimum one (1.95 eV). However, the results obtained with this material system encouraged the study of other QD-IBSC prototypes.

Some works have used analytical models to assess the potential of new QD systems [García-Linares'11]. These analyses have revealed that wide bandgap barrier materials (larger than the bandgap of the GaAs) are good candidates to implement QD-IBSC prototypes. So far, the most tested QD systems have been InAs/AlGaAs, GaAs/AlGaAs and InAs/InGaP. In general, these QD systems have led to a better distribution of the bandgaps showing, in particular, a higher E_L . The most remarkable results have been obtained in InAs/AlGaAs QDs. In this material system it has been possible, for the first time, to spectrally resolve the three optical transitions involved in the operation of IBSCs [Ramiro'14a; Tamaki'14]. Besides, also for the first time, the phenomenon known as "voltage up-conversion" has been proved, which consists of adding up the energy of two photons to produce electrical work. The two operating principles of IBSCs have been proved in InAs/AlGaAs QDs, but unlike the case of previous experiments in InAs/GaAs QDs, these principles have been evidenced in the same device. However, it must be mentioned that they have been proved under different conditions. On one hand, the two-photon absorption has been detected at cryogenic temperature by using illumination with a low irradiance level. On the other hand, the voltage-preservation has been detected at RT by using illumination with a high irradiance level [Ramiro'14a].

Although most research in IBSCs has been focused on QD-IBSC prototypes, there has been a parallel research line focused on prototypes fabricated using DLs and HMAs. The development of these technologies is recent because they have emerged in the context of the IBSC and have not received advantages from previous experience in the field of the material systems involved. So far, prototypes of HMAs have rendered promising results. The most remarkable one is the generation of sub-bandgap photocurrent densities by the

absorption of two-photon in IBSCs prototypes based on ZnTe:O⁴ [Tanaka'13] and GaAs:N [Ahsan'12]. This sub-bandgap photocurrent density has usually been higher than that produced in QD-IBSC prototypes. The research in IB materials based on DLs has not resulted as promising as in HMAs. In its initial stage, several theoretical works investigated different material systems to identify good candidates to implement IBSCs. Some materials such as GaAs:Ti and GaN:Mn were proposed and fabricated, showing some technological difficulties (Section 1.2.2). In these materials, sub-bandgap transitions have been detected [Sheu'13;Sonoda'12] but the IBSC operating principles have not been demonstrated yet. To deeply understand the limitations of these systems, well-known semiconductors such as Si have been studied. In spite of the limitations related to the low Si bandgap (~ 1.12 eV), this material has been useful to test some of the principles of the IBSC based on the insertion of impurities. In particular, the verification of the NRR suppression in materials based on Si:Ti has been reported in [Antolin'09].

Although the research in IBSC has produced several advances, two main problems still restrict the performance of IBSCs prototypes. The first one is the still inefficient sub-bandgap absorption and, the second one is the excessive voltage degradation of the IBSC prototype with respect to its reference cell. In general, these problems have impacted almost all IBSC prototypes, irrespective of their technology.

1.4 Scope and outline of the Thesis

We have reviewed in this Chapter the IBSC concept, its potential to provide high efficient solar cells and the current state of research in this field. The operation principles of the IBSC have already been demonstrated in different PV technologies, especially in QD-IBSC prototypes. However, practical IBSCs still need to overcome shortcomings responsible for poor performances and fulfill the operation principles under real life conditions. In this context, different IB materials and IB technological approaches need to be studied to increase the possibility of obtaining practical IBSCs. The main objective of this Thesis is to characterize IBSC prototypes that belong to the least investigated technologies based on the bulk approach. These IBSC prototypes can show suitable optical properties for PV applications that deserve to be investigated in depth. In addition, this Thesis contributes to the demonstration of the IBSC principles under conditions closer to working conditions, such as operation at room temperature. Finally, it seeks to expand the understanding of the behavior of actual IBSCs, increasing the research capabilities of the

⁴In this Thesis, when referring to HMAs we will use the notation X:Y where X is the semiconductor host and Y is the element introduced in small quantities. When referring to a bulk material with DLs, we will use the notation X:Y, where X is the semiconductor material and Y is the impurity atoms.

IES-UPM by implementing new characterization techniques. These techniques are capacitive techniques, which can provide information about recombination processes and complement the characterization obtained from optical techniques, focused on studying generation processes.

Chapter 2 is devoted to the study of IBSC prototypes based on ZnTe:O, which is a HMA capable of behaving as an IB material. These IBSC prototypes are studied in collaboration with the University of Michigan. The exhaustive characterization of these solar cells evidences the presence of three optical transitions, VB→IB, IB→CB and VB→CB. However, the operation principles of the IBSC are not proven. An insufficient oxygen concentration and a non-optimum band alignment seem to make this demonstration difficult.

In Chapter 3, IBSC prototypes based on the introduction of DLs inside the bandgap of host semiconductors are characterized. In particular, IBSC prototypes based on Si:Ti are studied in collaboration with the Universidad Complutense de Madrid and the Universidad Politcnica de Catalua. Sub-bandgap photocurrent is detected and associated to DLs introduced by Ti atoms. A tunneling-emission from the IB to the CB seems to obscure the effects of possible IB→CB optical transitions. As a consequence of this undesired emission, a reduction of the effective bandgap of the solar cells impedes the demonstration of the voltage preservation principle. IBSC prototypes based on GaAs:Ti are also studied in Chapter 3 in collaboration with the company RIBER (France). These solar cells fulfill the operation principles of the IBSC. However, energy levels introduced by Ti atoms are not responsible for this. Instead, the energy levels resulting from crystalline defects in GaAs grown at low temperature seem to be the cause of the processes predicted by the IB theory.

Chapter 4 contributes to the demonstration of the IBSC principles at room temperature. QD-IBSC prototypes are studied in this Chapter in collaboration with the University of Tokyo. Experimental results demonstrate the production of photocurrent by means of the absorption of two-photons, for the first time at room temperature. These two-photon photocurrent result in an absorption threshold that corresponds to E_L , which facilitates the demonstration that eV_{OC} surpasses the absorption threshold at room temperature, even under low irradiance conditions.

In Chapter 5 we present the implementation of an experimental set-up dedicated to the “Deep-Level Transient Spectroscopy” (DLTS) technique. A revision of the theory used by this technique allows us to expand the understanding about the features of the IB-states and its impact on the structure of practical devices. The experimental results obtained with this technique complement the results of previous Chapters. Particularly, these results give us information about the carrier-capture processes involving the IB of different materials, in terms of the capture cross sections of IB-states.

Finally, in Chapter 6, we compile the main results and conclusions of the Thesis, as well as suggestions that arise from this Thesis for future projects.

2 RESERACH ON IBSCs BASED ON ZNTE:O

2.1 Introduction

The electrical properties of semiconductors of the II-VI group, such as ZnTe, have been studied long before the IBSC concept was proposed (1997). Experimental results have shown that low concentrations of substitutional oxygen atoms (O_{Te}) in ZnTe, typically lower than 10^{18}cm^{-3} [Merz'71], cause the appearance of energy levels at 0.4 eV below the CB [Dietz'62; Hopfield'66]. Later, photo-reflectance measurements evidenced that the presence of O_{Te} in molar fractions around 1-5% not only introduce energy levels inside the ZnTe bandgap, but also modify the fundamental properties of ZnTe [Walukiewicz'00]. These materials are called highly mismatched alloys (HMAs) due to the large difference between the electro-negativity of O and Te ($\Delta X = 1.4$) [Yu'03]). The properties of HMAs are explained by the band-anticrossing model (BAC), which establishes that the interaction between the localized states associated with O atoms and the extended states of the ZnTe semiconductor leads to the split of the CB band into two sub-bands, E_+ and E_- (illustrated in Fig. 1.9b) [Walukiewicz'00]. According to BAC model, the relative position of these two energy bands respect to the VB follows:

$$E_{\pm} = \frac{1}{2} \left\{ (E_M + E_0) \pm \sqrt{(E_M - E_0)^2 + 4xC_{MO}^2} \right\} \quad (2.1)$$

where E_0 is the energy of the localized O level, E_M is the energy of the conduction band states of the ZnTe matrix, C_{MO} is the matrix element describing the coupling between localized and extended states, and x is to the composition of the $\text{ZnO}_x\text{Te}_{1-x}$ alloy.

Since the extended states of the energy band E_- can behave as an IB, ZnTe:O could be a good candidate to implement IBSCs. The fabrication of the first HMAs based on $\text{ZnTe}_{1-x}\text{O}_x$ was reported in [Yu'03], by using O ion implantation followed by pulse laser melting (PLM). The combination of these techniques allowed O molar concentrations in the $x = 0.01 - 0.04$ range, which were well above the O solubility limit in ZnTe (10^{17}at/cm^3 [Burki'90]). In order to increase the stability of O_{Te} , Mn atoms were added to some samples ($\text{Zn}_{1-y}\text{Mn}_y\text{Te}$). The experimental results carried out in these HMAs have shown that, for the case of $\text{Zn}_{0.88}\text{Mn}_{0.12}\text{O}_{0.01}\text{Te}_{0.99}$, the energy band structure of the material was characterized by $E_G = 2.56 \text{ eV}$, $E_H = 1.83 \text{ eV}$ and $E_L = 0.73 \text{ eV}$. This configuration is not the optimal one to fabricate an IBSC (see Section 1.1.2) because it leads to a limiting efficiency of 45 % under 6000 K black body radiation and maximum sunlight concentration [Yu'03]. However, this efficiency is higher than the SQ limit for conventional solar cells under the same illumination conditions and bandgap E_G , and it could be increased by varying the composition of the HMA. For example, in theory, a composition of $x = 0.02$ would lead to an efficiency limit of 56% [Yu'03].

Other growth techniques to fabricate ZnTe:O materials have been investigated [Merita'06;Wang'09a]. One of them was the MBE technique used by the group of Prof. Jamie Phillips, at the University of Michigan. In this technique, the presence of an oxygen partial pressure into the growth chamber allowed O atoms to be incorporated into the ZnTe lattice. To prevent the formation of O bubbles, low growth temperatures were used (250°C compared to the typical temperatures in the $300\text{-}400^\circ\text{C}$ range [Kuhn'91]). The ZnTe:O obtained showed some of the expected features of IB materials, with energy states 0.5 eV below the CB [Wang'09b]. These materials were used to fabricate IBSCs prototypes in which it was possible to demonstrate some of the operating principles of IBSCs based on HMAs. In particular, it was possible to relate the presence of O_{Te} atoms with an extended solar cell spectral response, and an increase in short circuit current and in power conversion efficiency. In addition, the generation of electrical power was achieved by illuminating with two sub-bandgap optical excitations [Wang'09b].

The results summarized above serve as a basis for the research in IBSCs based on ZnTe:O. In this Chapter we will contribute to this research by means of the experimental characterization of several batches of ZnTe:O materials and their corresponding IBSC prototypes. These devices are the result of the collaboration between the University of Michigan and the IES-UPM.

2.2 Description of ZnTe:O materials and corresponding IBSC prototypes

The ZnTe:O materials and their corresponding IBSC prototypes studied in this Chapter have been designed and manufactured at the University of Michigan using a MBE reactor (Riber 32 system). Different growth recipes have resulted in a total of twenty seven material structures and eighteen device structures, where several practical problems related to the immaturity of this technology have been fought with more or less success.

ZnTe is a II-VI semiconductor with a direct bandgap of around 2.29 eV and a “zincblende” crystal structure with a lattice constant of 6.1 Å [Potlog'12]. Wide bandgap II-VI semiconductors show an asymmetry between the n and p dopability, so they usually exhibit a pronounced preference for only one type of doping [Zhang'98]. This is the case of ZnTe, which is normally p-type because a self-compensation effect (related to the presence of Zn vacancies) appear when this material is doped with donor impurities [Title'64]. Consequently, the formation of the p-n junction in ZnTe homo-junction solar cell is practically impossible. In this context ZnTe hetero-junction solar cells have been proposed as an alternative [Potlog'11]. In this Chapter, this kind of structures are used to manufacture IBSC prototypes. The emitters (n-emitter and p-emitter), the IB material and the substrate of these cells are based on the materials described below:

- **Emitters:** ZnTe was used to fabricate p-emitters because of its ability to be p-type doped with N in a controlled way, with hole concentrations of up to 10^{20} cm^{-3} [Baron'98]. In these layers N was incorporated using plasma source. ZnSe was used to fabricate zincblende n-emitters because of the ability of this material to be highly n-type doped with Cl. Fig. 2.1 illustrates that ZnSe has a bandgap of 2.7 eV (higher than ZnTe) and it exhibits a significant lattice mismatch to ZnTe (8%). For this reason, continuous efforts were carried out to improve the growth procedure at the ZnSe/ZnTe interface. At times, these procedures resulted in abrupt interfaces (without buffer layer) and in other cases in ZnSe/ZnTe graded alloys.

Fig. 2.1: Representation of bandgap energy as a function of the lattice constant for main II-VI (in magenta and orange colors) and III-V (in blue and green colors) semiconductors. This image was obtained from http://asumbe.eas.asu.edu/images/research/multijunction/Colorspectrum_Eg_a.jpg/, accessed on 2016-05-11. (Archived by WebCite® at <http://www.webcitation.org/6hQEccwny>).

- **IB material:** In all the material and device structures in this Chapter, the IB material has been based on ZnTe:O. In this IB material, the epitaxial ZnTe layers were grown with a beam flux ratio of $\text{Te}/\text{Zn} \approx 2$. The O atoms were incorporated inside these layers by a plasma source in molar concentrations of around 0.5%, according to SIMS measurements [Phillips'13]. In order to avoid the formation of clusters of O during the growth, the temperature of the substrates was set at 250°C. The resulting ZnTe:O material maintained the p-character of ZnTe, which is to be expected since O is an isovalent impurity when the O is Te-substitutional.
- **Substrate:** At the University of Michigan, ZnTe substrates were not available for growth. This made it necessary to use substrates of different materials, which lead to the possibility of lowering the costs of this technology by using lower cost substrates such as GaAs (in comparison to ZnTe substrates). GaAs (001) substrates were used with reasonable success in spite of the 7% lattice mismatch with respect to ZnTe.

The structure of the devices studied in this Chapter was completed at the University of Michigan, using standard metallization and liftoff processes to obtain a wire grid top contact and bottom metal contacts. For the sake of simplicity, window layers and anti-reflecting coatings were not included in the structures, which were not optimized in terms of thicknesses, doping levels, etc. The reason for using this simple structure was to demonstrate the operating principles of IBSCs, not the fabrication of highly efficient ZnTe solar cells.

The material and the device structures provided by the University of Michigan have been characterized at IES-UPM using optoelectronic techniques. The most remarkable results have been provided by the material and the device structures shown in Fig. 2.2. These results will be detailed in Section 2.4.

Fig. 2.2: Layer structure of IB materials (R814) and IBSC prototypes (R390 and R1030) in which the width and the semiconductor material of each layer are specified. The type of doping is indicated by colors (color red corresponds to p-type and color blue corresponds to n-type).

In order to evaluate the impact of the presence of the IB, reference samples were fabricated with the same structure as those shown in Fig. 2.2, except for the presence of O. The reference solar cells for samples R814, R390 and R1030 were designated as R815, R389 and R1024 respectively.

At first, research on this kind of samples have tried to reproduce previous results obtained by the University of Michigan [Wang'09b]. Then, our research has focused on evaluating the capability of IBSC prototypes based on ZnTe:O to fulfill the theoretical operating principles. These studies have shed light on the absorption coefficients of the sub-bandgap transitions of this material and some practical aspects that can limit the performance of the solar cells studied.

2.3 Characterization of IBSCs based on optoelectronic techniques

Throughout this Thesis different characterization results of IBSC prototypes will be discussed, hence it is important to briefly present the techniques employed to obtain them. Some of these techniques have been traditionally used in PV and others have been expressly developed for IBSC characterization. In order to approach the IB-related behavior, these techniques analyze the presence of sub-bandgap electronic transitions, study the extraction of carriers generated by the absorption of sub-bandgap photons or test the electrical power production.

2.3.1 Presence of sub-bandgap electronic transition

The presence of an IB inside the bandgap of a semiconductor material makes it possible for additional electronic transitions to take place. In these transitions electrons can gain or cede part of their energy. Depending on the elements involved in this energy exchange, different experimental techniques can be applied to study the sub-bandgap transitions VB-IB and IB-CB. For example, if electrons exchange their energy with photons, electroluminescence (EL) and photo-luminescence (PL) measurements can be used to study the recombination processes (labelled as r_{VI} and r_{IC} in Fig. 1.2), and PR and absorption measurements can be used to study generation processes (labelled g_{VI} and g_{IC}). We will describe here the PL and the absorption techniques employed in this Thesis to detect sub-bandgap transitions.

Luminescence techniques consist of measuring the spectrum emitted by materials and devices. In particular, in PL measurements, the luminescent spectrum arises from de-excitation processes that take place after samples are illuminated with supra-bandgap photon energies. The luminescent spectrum of an ideal IB material or an ideal IBSC can show three distinct peaks related with de-excitation processes involving the three energy gaps E_L , E_H and E_G . The presence of luminescent peaks related to any of the two sub-bandgaps, E_H or E_L , is sufficient evidence of the existence of intermediate states that optically interact with the VB, the CB or both.

The absorbance spectrum (A) is obtained indirectly from the measurements of the specular reflectance (R) and transmittance (T) spectra, through the relation: $A = 1 - T - R$ ⁵. The absorbance provides information about the strength of the generation processes, which depend on the thickness of the samples and the absorption coefficients. The energy

⁵ The formula $A = 1 - T - R$ is valid if there is not light scattered from the surfaces of the samples. This condition can be considered true, for example, in MBE samples grown on substrates with both sides polished.

threshold of the absorbance determines the lowest photon energy that can be absorbed. For this reason, in IB materials and IBSCs, this threshold can correspond to E_L , as illustrated in Fig. 2.3. From this figure it can be deduced that, in general, only α_{IC} can be clearly determined for the $E_L < E < E_H$ energy range because at this range only one absorption transition is possible, the IB $\rightarrow$ CB transition.

Fig. 2.3: Absorbance for an IB material with an infinite thickness and selective absorption coefficients (left side) or non selective absorption coefficients (right side). The number of possible transitions is indicated for each energy range, $E_L < E < E_H$, $E_H < E < E_G$ and $E_G < E$.

2.3.2 Extraction of carriers generated by sub-bandgap excitation

The collection of generated carriers in a solar cell can be studied by means of spectral photocurrent measurements. These measurements can be directly expressed as a spectral response (SR) or they can be transformed into external quantum efficiency (EQE). In both cases the measured photocurrent corresponds to the illumination with monochromatic light that comes from the output of a monochromator. Inside the monochromator, the light of a broadband spectrum source is diffracted and, at the output, appropriate optical filters are placed to block the harmonic components and guarantee the monochromaticity of the photon beam. The intensity of the monochromatic beam is modulated by using an optical chopper, and the alternate photocurrent generated by the cell in response to this illumination is measured with a lock-in amplifier. The photocurrent measurements presented in this Thesis are applied to device structures which are biased at 0 V to assure the photovoltaic origin of the signal.

Fig. 2.4 Sketch of the optical elements used in a QE set-up to illuminate an IBSC: (a) without light bias, (b) with a light bias whose energy is in the range $E_L < E < E_H$ and (c) with a light bias whose energy is in the range $E_H < E < E_G$. The QE curves corresponding to ideal IBSCs with selective absorption coefficients (g) and non selective absorption coefficients (h and i) are plotted in (d), (e) and (f) respectively. In these graphs the black, red and green curves correspond to the illumination condition of the cases (a), (b) and (c) respectively [López'03].

In ideal IBSCs, the absorption coefficients should be selective, which implies that photons with a specific sub-bandgap energy can only be absorbed in VB→IB or IB→CB transitions. To generate sub-bandgap photocurrent, it is necessary for both sub-bandgap transitions to take place. Hence, it is necessary to illuminate the IBSCs with two different photon energies, one that guarantees the VB→IB transition and another that guarantees the IB→CB transition. For this reason, during photocurrent measurements, IBSCs are usually illuminated by the monochromatic light that comes from the monochromator output and by a bias light. This bias is usually also a monochromatic light, whose photon

energies correspond to $E_L < E < E_H$ or $E_H < E < E_G$. This is depicted in Fig. 2.4, where the QE measurement of an IBSC with ideal selective absorption coefficients is compared to two examples in which absorption coefficients are non selective [López'03]. In Fig. 2.4 the impact of non-radiative generation processes has been omitted.

2.3.3 Electrical power production: Principle of voltage preservation

The simplest experimental technique used to evaluate the electrical power production consists of measuring the $J - V$ characteristic of the solar cells.

In particular, in IBSCs, the IB should not limit the voltage of the $J - V$ characteristic. The easiest way to demonstrate this is to measure the V_{OC} of the cell, which, multiplied by the electron charge, has to be higher than any of the two sub-bandgaps, E_L and E_H . This experiment can be carried out using the experimental technique detailed in [Linares'12] where concentrated white-light and low temperatures are used to induce an output voltage in the cell as high as possible. In this technique, the light of a xenon flash lamp is concentrated by a lens to illuminate the cells with different irradiances during the flash discharge. Under these conditions, two kinds of measurements can be obtained: $J - V$ and $J_{SC} - V_{OC}$ curves at different irradiances. During these measurements, the samples are placed in a closed-cycle He cryostat to lower the temperature. In Fig. 2.5 a sketch of this technique is depicted.

In the $J - V$ curve each point is measured in a single flash pulse. Hence, it is necessary to use as many flash pulses as points are desired to plot the curve. During each flash pulse, samples can be biased at a fixed voltage by using a 4-wire source meter, or they can be biased at different voltages during the same flash pulse by connecting a resistor in series. In order to ensure that every point of the $J - V$ curve is obtained under the same irradiance, a Si detector is used to monitor the level of illumination (for more details see [Linares'12]).

In the $J_{SC} - V_{OC}$ curve each point corresponds to a different irradiance level. To obtain this curve, only two flash pulses are required. During the first flash pulse, samples operate at open-circuit, so that V_{OC} values at different irradiances are obtained as the intensity of the light of the flash decays. During the second flash pulse, samples are biased at 0 V by using a 4-wire source meter, and J_{SC} at different irradiances is obtained. The correlation between these two sets of data is obtained with the Si reference detector (for more details see [Linares'12]).

It is worth noting that in these measurements the Si detector cannot be used to determine the sunlight concentration factor, X . This is because the detector is placed close to samples but not at an identical position, so that the irradiance impinging on the detector

and sample is different. In this context, the concentration factor is estimated by dividing the measured photogenerated-current density (J_L) in the solar cell under study by the value of J_L corresponding to one sun, that can be known from the $J - V$ characteristic of the solar cell at one sun.

Fig. 2.5: (a) Sketch of the experimental technique used in [Linares'12]. The procedure to obtain $J - V$ curves and $J_{sc} - V_{oc}$ curves at different irradiance levels is illustrated in (b) and (c) respectively and is detailed in [Linares'12].

2.4 Experimental results of IBSC prototypes based on ZnTe:O

2.4.1 IBSC operating principles

Previous to this Thesis, other research groups reported experimental results relating to ZnTe:O samples. For example, PL and PR measurements evidenced optical transitions below the bandgap, at 1.8 eV, which distinctly differ from the fundamental

bandgap transition (~ 2.32 eV) [Wang'09b;Yu'03]. Capacitance-voltage measurements based on materials grown under similar conditions to those studied here indicated a p-type background $< 10^{16} \text{ cm}^{-3}$ [Wang'10]. According to these previous results, a band diagram as the one depicted in Fig. 2.6 is expected for the IB material studied in this Chapter. In this diagram, the collection of the intermediate states is represented as an IB termed E_- (in agreement with the nomenclature used for the HMAs), which is expected to be almost empty under equilibrium.

Fig. 2.6: Band diagram for ZnTe:O IB material. The values for E_L , E_H and E_G can vary depending on the O concentration. Since in this material we can assume the IB to be empty of electrons under equilibrium, the sub-bandgaps E_L and E_H are not defined with respect to the middle of the band E_- (or IB), but they are defined for convenience respect to its bottom.

Optoelectronic techniques were used at the IES-UPM to study the presence of intermediate states⁶ in the material structures provided by the University of Michigan. One of the most evident results was obtained in the material structure R814 (Fig. 2.2). In this sample, absorbance measurements could not be used to study the VB-IB transition because the GaAs substrate absorbs the light in that same energy range. For this reason, we limited ourselves to measure the reflectance spectrum of sample R814 and its corresponding reference structure R815. These reflectance spectrums (Fig. 2.7) were obtained by illuminating the front side of the samples with the monochromatic light that came from the output of a 1/4 m monochromator. The intensity of the light reflected by the samples was measured by a calibrated Si detector to determine its spectrum ($S_{R,\text{sample}}$). The same procedure was repeated by illuminating a gold surface, obtaining the spectrum of the light reflected by gold ($S_{R,\text{gold}}$). The $S_{R,\text{gold}}$ was used to calibrate the spectrum of the incident light (S_I), since gold has a known spectral reflectivity. So finally, the reflectance of the samples could be calculated using the expression, $S_{R,\text{sample}} / S_I$.

⁶ We will refer to the intermediate states of the ZnTe:O materials as E_- (following HMA nomenclature) or as IB (in the context of IBSCs).

Fig. 2.7: Measurements of the spectral reflectance of ZnTe (R815) and ZnTe:O (R814) samples. The reflectance was measured at 30° respect to the normal incident. In the graph, the bandgap of ZnTe is specified for reference (after [Antolín'14]).

In Fig. 2.7 two reflectance patterns can be identified, a flat reflectance at high energies and a reflectance with interference oscillations at low energies. In the ZnTe sample (black curve), the change in the reflectance pattern is produced at the bandgap energy. This phenomenon has been typically observed in semiconductor films and it has been associated to the absorbance of the semiconductor, as illustrated in Fig. 2.8. According to this figure, a flat reflectance is obtained if the light is absorbed in the upper semiconductor film. In this case, the light is only reflected on the surface so the reflected light is constituted by the component R_1 of Fig. 2.8. If light is not absorbed in the semiconductor film, light can be reflected not only on the surface, but also on the interface ZnTe(O)/GaAs. This produces a Fabry-Pérot interference pattern because the additional components ($R_2 \dots R_n$) can also contribute to the reflectance.

Fig. 2.8: Light beam components present in the reflectance experiments. On the left, photons with energy below the bandgap of ZnTe(O) are reflected at the ZnTe(O)/GaAs interface. This reflection produces an interference pattern which result in a reflectance with oscillations as a function of the photon wavelength. On the right, photon with energy above the bandgap of ZnTe(O) are absorbed completely at the ZnTe(O) layer. This implies that photons are only reflected on the surface, which results in a flat reflectance. (after [Antolín'14])

In the case of ZnTe:O (red curve in Fig. 2.7), the oscillations of the reflectance signal are strongly attenuated at sub-bandgap energies (below 2.25 eV), which indicates that absorption processes are produced for those photon energies. This attenuation is much lower in the reference sample (black curve in Fig. 2.7), so the sub-bandgap absorption processes may be related to the presence of O and the presence of an IB [Antolín'14]. From the measurements of Fig. 2.7, the value of the absorption coefficient associated to sub-bandgap transitions can be estimated up to 10^4 cm^{-1} at photon energies between 2 eV and 2.25 eV. This value is in agreement with previous reports [Tooru'11].

From the measurements plotted in Fig. 2.7 it is not possible to clearly determine the IB position inside the ZnTe bandgap. On one hand, the attenuation of the reflectance signal for sub-bandgap energies is very progressive. On the other hand, the measurements do not distinguish between absorption processes related to VB→IB transitions and absorption processes related to IB→CB transitions. PL measurements were carried out to intend to spectrally resolve the IB. The PL measurement of Fig. 2.9 corresponds to the material structure R863, which is similar to the R814 sample. This measurement shows a sub-bandgap luminescent spectrum, obtained at 298 K under illumination with photons of 3 eV coming from a diode laser. This sub-bandgap luminescence evidences the existence of two sub-bandgap transitions. The peak related to emission of photons with energies around 1.5 eV can be associated to the bandgap of the GaAs substrate, while the peak around 1.8 eV can be associated to radiative recombination processes from the IB to the VB. This measurement determined the position of the IB at around 1.8 eV above the VB.

Fig. 2.9: Sub-bandgap PL spectrum of the material structure R863, based on a ZnTe:O layer grown on a semi-insulating GaAs substrate. Two distinct luminescent peaks appear. One of them is attributed to the GaAs substrate and the other is associated to radiative recombination processes between the IB and the VB (Courtesy of Dr. Íñigo Ramiro).

Once the presence of intermediate states has been identified in these material structures, we can study the impact of these states on the operation principles of IBSC prototypes. This was studied for the first time in [Wang'09b]. In that work, an extended spectral response was detected in the IBSC prototype, which was associated to intermediate states located at 1.8 eV above the VB of the ZnTe:O. To reproduce this result, we measured the spectral response of the IBSC prototype R390 and its corresponding reference solar cell R389, with identical structures (Fig. 2.2) to those reported in [Wang'09b]. The spectral response measurements were transformed into EQE using calibrated detectors in the 0.7-3.5 eV range. The results are shown in Fig. 2.10 where sub-bandgap response has been detected in both samples without using any light bias.

Fig. 2.10: Measured EQE of IBSC prototype R390 (red curve) and its corresponding reference solar cell R389 (black curve) at room temperature and without light bias. Dashed lines mark the experimental bandgap for ZnTe (extracted from the abrupt decay in the EQE of the reference solar cell at 2.25 eV) and the photon energy that corresponds to the maximum EQE for the IBSC prototype (1.74 eV).

The EQE of the reference solar cell R389 should be negligible for photon energies below the ZnTe bandgap (2.25 eV). The reason for that is that, in spite of sub-bandgap photon being able to generate carriers in the GaAs substrate, these carriers should not be extracted due to the large VB-offset between the n-GaAs and p-ZnTe (see Fig. 2.11). This VB-offset should block the transfer of minority carriers generated in the n-GaAs substrate. However, the experimental results proved that this blocking was not effective, because a significant photo-response was produced when the reference solar cell was illuminated with sub-bandgap photon energies in the 1.4 to 2.25 eV range. This ineffective blocking could be due to the presence of energy states inside the bandgap that facilitate the tunneling of carriers (as depicted on the right in Fig. 2.11). These states could be related to the formation of a quantum well at the ZnTe/GaAs interface or the presence of defects due to the lattice mismatch between ZnTe and GaAs. Crystalline defects could also be the reason why the EQE measurements show a poor overall efficiency and an extreme degradation of the front emitter.

The EQE of the IBSC prototype shows a sub-bandgap response higher than that of the reference cell, with a significant peak centered at 1.74 eV. This energy is similar to the energy of the intermediate states introduced by the presence of O atoms. Then, it seems reasonable to relate this peak to the intermediate states inside the ZnTe bandgap, which we will refer to as IB. According to this hypothesis, the sub-bandgap response could be produced by two pumping processes in which sub-bandgap photons excite electrons from

VB to IB and from IB to CB. This would mean that absorption coefficients are non selective (as illustrated in Fig. 2.4) and suitable for PV applications since they lead to sub-bandgap EQE values as high as 7%. However, in view of the band diagram of the IBSC prototype (depicted in Fig. 2.11), carriers could also be transferred from the IB to the CB by non-optical mechanisms. These mechanisms are represented in red in Fig. 2.11 and can be related to thermionic emission or tunnel-effect processes.

Fig. 2.11: Band diagram of the IBSC prototype R390 under equilibrium (obtained with SCAPS). The energy band alignment provides a large VB offset that blocks the carrier transfer from GaAs to ZnTe:O (left side). This blocking can be ineffective if energy levels are introduced inside the bandgap (right hand). It is expected that the IB is almost empty of electrons, except for the portion which is inside the space charge region and close to the GaAs interface. At this portion, the proximity between the IB and the CB of GaAs can facilitate the appearance of a non-optical excitation mechanism (illustrated by the red arrow).

Subsequent IBSC prototypes were fabricated including new structural elements to eliminate the contribution of GaAs to the photocurrent and reduce the impact of non-optical transfer mechanisms from the IB to the CB. The growth of ZnSe n-emitter on the GaAs substrate and the subsequent ZnTeSe buffer layer aimed to reduce the contribution of the substrate. The growth of ZnTe barrier layers grown at both sides of the ZnTe:O layer aimed to avoid non-optical transfer mechanisms. These structural changes led to different EQE results. As a representative example, we will show the results obtained in the IBSC prototype R1030 and its corresponding reference solar cell R1024 (Fig. 2.2).

The EQE of these solar cells was obtained under similar experimental conditions to previous results, except for, in this case, a He-Ne laser (633nm/30mW) was used to illuminate continuously the IBSC prototype during one of the measurements. The results are shown in Fig. 2.12 (top), using the same scale as in previous results to facilitate comparison.

Fig. 2.12: EQE of IBSC prototype R1030 (red curve) and its corresponding reference solar cell R1024 (black curve) measured at room temperature. The plot on the top shows the EQE in linear scale and the plot on the bottom shows the EQE in logarithmic scale for the sub-bandgap spectral range. In both cases, the dashed red line was obtained by using a He-Ne laser power of 30mW to illuminate the IBSC prototype with 1.95 eV photon energies. It is expected that this laser illumination photo-fills the IB through transitions $VB \rightarrow IB$, providing the carriers to be pumped by the transition $IB \rightarrow CB$. For reference, black dashed lines marks the experimental bandgap value for ZnTe, the energy corresponding to the IB and the photon energy of the light bias.

In Fig. 2.12 the photocurrent generated in the GaAs substrate was only observable using the logarithm scale used in the bottom plot (from 1.4 eV to 1.9 eV). Prior to this, the

GaAs contribution was observable using a linear scale, as seen in Fig. 2.10. The significant reduction of the photocurrent generated in the substrate can be attributed to the reduction of interface defects in samples R1024 and R1030 due to a better lattice match between the GaAs and the semiconductor layers grown on it. This is supported by the fact that a higher EQE is obtained in these samples (compared to samples R389 and R390), in particular at high energies, which indicates the improvement in the crystal quality of the overall device.

The solid red curve in Fig. 2.12 shows the EQE of the IBSC prototype R1030 measured without using light bias. Under these illumination conditions, the IBSC prototype R1030 did not provide any significant sub-bandgap response with respect to the reference solar cell R1024. This result differs from the result obtained with the previous IBSC prototype R390 (solid red line of Fig. 2.10), in which part of the sub-bandgap response was associated to the presence of an IB. We can assume that the suppression of this sub-bandgap response in the R1030 sample is due to the structural modifications mentioned. These modifications increase the physical separation between the IB and the CB of the n-emitter in sample R1030, which can be observed in the band diagram of Fig. 2.13. Therefore, we can suppose that the IB was not isolated from the CB in the R390 sample, unlike sample R1030 where the IB was isolated.

Fig. 2.13: Band diagram of the IBSC prototype R1030 under equilibrium (obtained with SCAPS). The ZnSe n-emitter on GaAs substrate and the subsequent ZnTeSe buffer layer reduce the contribution of the substrate to the photocurrent. ZnTe barrier layers at both sides of the ZnTe:O layer provide isolate the IB from the CB by increasing the separation between these energy bands. In this IBSC prototype the IB is totally empty.

If the IB is properly isolated in sample R1030, it should be possible to demonstrate the generation of two-photon photocurrent in this sample, as long as the IB is partially filled. However, in the IBSC prototype R1030 the IB was expected to be empty under equilibrium. This IB can be partially filled by illuminating continuously the sample with 1.95 eV photons, coming from a He-Ne laser of 30 mW power. This procedure was used to obtain the EQE measurement represented by the dashed red curve in Fig. 2.12. As can be

appreciated from this curve, the mentioned illumination conditions were not enough to detect sub-bandgap response related to optical transitions through the IB. The reason could be insufficient photo-filling, a low rate of transitions $IB \rightarrow CB$ or a high rate of recombination between the IB and the CB.

Fig. 2.14: (Top) The reflectance and transmittance spectra measured with FTIR on the ZnTe:O (left) and ZnTe (right) samples. (Bottom) The absorption coefficient extracted from these spectra. The IB-CB transition is identified in ZnTe:O at around 0.4 eV (after [Antolín'14]).

To study the absorption coefficient of the transition $IB \rightarrow CB$, α_{IC} , a Fourier transform infrared (FTIR) spectrometer was used to measure the absorbance of samples R814 and R815 (Fig. 2.2) at room temperature. The results were obtained in the 0.2-1 eV range (below the bandgap of the GaAs substrate), by using a broadband spectrum to continuously illuminate the samples. Since this spectrum contained those wavelengths

that produce VB-IB transitions in ZnTe:O, the IB could be photo-filled with a sufficient carrier population to allow the measurement of the IB-CB transitions.

From Fig. 2.14 (top) it can be appreciated that the specular reflectance (R) and transmittance (T) spectra of both samples show interference oscillations. These oscillations were the result of the interference patterns previously explained in Fig. 2.8, produced by reflections on the interface ZnTe(O)/GaAs and on the front surface. From these oscillations the thickness of the samples was estimated to be $3.5\ \mu\text{m}$ for the ZnTe film and $4.0\ \mu\text{m}$ for the ZnTeO film, using the well-known fact that in the interference pattern T reaches a maximum and R a minimum when $2nd \approx m\lambda$ (n is the refractive index, d is the thickness of the film, λ the wavelength, and m an integer). In these calculations it has been assumed that ZnTeO and ZnTe have the same n .

The dip around $0.4\ \text{eV}$ in the transmittance of the ZnTe:O sample is not present in the ZnTe sample (Fig. 2.14). This feature can be interpreted as the effect of the absorption of photons in IB-CB transitions because only this transition can take place for the energy range used. From the reflectance and transmittance spectra, we obtained the absorbance A , and consequently the absorption coefficient from the expression $A = 1 - \exp(-\alpha d)$. The resulting absorption coefficients are shown in Fig. 2.14 (bottom). In this figure the absorption coefficient of both samples show the same baseline, which suggest some level of inaccuracy in the measurements introduced by the scattering of light by non-flat surfaces. A peak is observed at $0.3\text{--}0.4\ \text{eV}$ for ZnTeO, clearly above the amplitude of the interference oscillations. This peak can be associated to the IB-CB absorption coefficient, α_{IC} , reported for the first time in [Antolín'14]. It is worth mentioning that this absorption coefficient shows an abrupt selective character, since for energies higher than $0.5\ \text{eV}$ the absorption coefficient does not surpass the baseline. The selectivity of the absorption coefficient could seem to be a positive feature from the point of view of IBSC implementation. However, if the absorption coefficients are delta-shaped instead of box-shaped (illustrated in Fig. 2.15), as occur in this case, the limiting efficiency of the IBSC could be similar to the corresponding SQ limit for conventional solar cells because few sub-bandgap photons could be absorbed.

In general, absorption coefficients increase with the number of states and the overlapping between the electron wave functions involved in optical transitions. In the CB the density of states increases with the energy. For this reason we can interpret the decrease of α_{IC} for energies higher than $0.4\ \text{eV}$ as indicative that the overlapping between the wave functions for states in the IB and the CB decreases for CB-states above the bottom of the CB. This fact suggests that IB-CB transitions occur between localized states in the IB and localized states at the bottom of the CB, as illustrated Fig. 2.15 (b).

Fig. 2.15: Representation of excitation processes between energy states of the IB and the CB (red arrows), the VB and the IB (green arrows), and the VB and the CB (blue arrows), and its corresponding absorption coefficients α_{IC} , α_{VI} and α_{VC} for two cases: (a) the case in which the wave function of all energy states is delocalized (black color) and (b) the case in which the wave function of the states in the IB and some states in the VB and the CB are localized (red color).

The presence of localized states in the IB could indicate that the O_{Te} concentration in the ZnTe:O layers is not high enough to form a real IB. This hypothesis is supported by the fact that E_G of the IBSC prototype R1030 is the same as the ZnTe bandgap of the reference solar cell R1024 (2.25 eV). According to the BAC model, for ZnTe:O materials, the values of E_G should increase with the O molar concentration, following the dependence described by equation (2.1) (illustrated in Fig. 2.16). However, as we have just mentioned, this is not the case. Besides, the absorption measurements of Fig. 2.14 have determined that the IB is placed around 0.4 eV below the CB, which matches with the position of the energy levels introduced by the presence of O_{Te} atoms in low concentrations inside ZnTe semiconductors [Dietz'62]. SIMS measurements have revealed that the maximum O concentration in these sample is about 10^{19} cm^{-3} . This concentration is lower than the O_{Te} concentrations of $\sim 10^{20} - 10^{21} \text{ cm}^{-3}$ that theoretically lead to the formation of an IB [Tablero'10]. This could be the reason explaining why the intermediate energy levels do not form a real IB. Furthermore, a portion of the O atoms could form oxygen pairs or oxygen clusters instead of substituting Te atoms of the semiconductor lattice, which would make it more difficult to obtain a true IB. In order to obtain practical IBSCs based on ZnTe:O, we consider that it is necessary to increase the O_{Te} concentration in the ZnTe:O

layers. This increase would result in blue-shift of the E_L , as predicted by the BAC model and evidenced experimentally in [Tanaka'12;Yu'03].

Fig. 2.16: Band diagram for ZnTe:O material with respect to the O mole fraction, x . The values of E_- and E_+ are calculated according to the BAC model described by the equation (2.1), assuming C_{MO} is 3.5 eV [Yu'03].

In Fig. 2.14 the absorption coefficient α_{IC} reaches a maximum value of 750 cm^{-1} , which could be reduced to 450 cm^{-1} if the value of the baseline is subtracted. This value is around two orders of magnitude lower than the absorption for the VB-IB transition estimated previously, which is not surprising taking into account that in p-ZnTe:O the IB is expected to be empty in equilibrium. Since the rate of IB $\rightarrow$ CB transition increases with the electron concentration in the IB [Shockley'52], increasing the IB photo-filling by illuminating the samples with high irradiances could increase the strength of the sub-bandgap transitions and improve the efficiency of the IBSC prototypes.

The $J - V$ characteristics of the IBSC prototype R1030 and its corresponding reference solar cell R1024 were measured under different illumination conditions (Fig. 2.17). $J - V$ curves under moderate irradiance conditions were obtained by illuminating the samples with the light of a xenon lamp after passing through AM1.5D filters. The curves under high irradiance conditions were obtained following the experimental technique described in Section 2.3.3, using a MgF_2 lens to focus the light of a xenon flash on the samples.

Fig. 2.17: $J - V$ characteristics of the reference solar cell (black) and the IBSC prototype (red). The curves of the plot at the top were obtained by illuminating the solar cells with AM1.5D spectrum. For the plot at the bottom, high irradiances were used to illuminate the reference solar cell with a concentration factor X_1 and the IBSC prototype with a concentration factor X_2 . In this case low temperatures of 77 K were used to induce output voltages as high as possible.

At the top of Fig. 2.17, the $J - V$ characteristics of the reference solar cell and the IBSC prototype were obtained under the same illumination conditions. The irradiance used to illuminate the solar cells was estimated at $90 \text{ mW}\cdot\text{cm}^{-2}$ (corresponding to AM1.5D spectrum) by means of a calibrated GaAs solar cell. This made it possible to obtain the conversion efficiency for both the reference solar cell (0.63%) and the IBSC prototype (0.34%). Nevertheless, under high irradiance conditions (Fig. 2.17 bottom) the efficiency of solar cells could not be obtained because the irradiances used in this case could not be

calibrated. As is explained in Section 2.3.3, under high irradiance conditions the concentration factor for the reference solar cell (X_1) and the IBSC prototype (X_2) is estimated by dividing the measured J_L by the J_L corresponding to one sun. However, in these devices J_L could not be obtained due to the impact of high series resistances and the break-down of the devices at reverse voltages (low shunt resistances were discarded in view of the dark $J - V$ measurements, which are not shown here). As a consequence X_1 and X_2 , which were not necessarily the same, could not be determined. However, a lower bound for these concentration factors could be obtained by dividing the measured J_{SC} by the value of the J_{SC} at one sun, which resulted in $X_1 > 226$ and $X_2 > 167$.

The presence of high series resistances could be the reason for the poor performances, the bad fill factors (FF) and the low J_{SC} obtained with these devices⁷. A priori, V_{OC} is not affected by the presence of series resistance. This voltage is ultimately limited by E_G/e , however, non-radiative losses, mismatch between the acceptance angle of spontaneous emission and the solid angle subtended from the source of light and energy losses from electrical contacts usually lead to V_{OC} lower than E_G/e . Experimentally, it has been observed that the V_{OC} of IBSCs can reach E_G/e , when cells operate at low temperature and under concentrated sunlight [García-Linares'12;García-Linares'13a]. These experimental conditions were used to measure $J - V$ characteristics (curves with square dots in Fig. 2.17). Under these conditions the maximum V_{OC} obtained for the IBSC prototype was 1.8 V. This value clearly exceeds the sub-bandgap E_L (0.4 eV) but not the sub-bandgap E_H , whose value is expected to be around 1.8 eV. Therefore, we cannot demonstrate the voltage preservation principle in the IBSC prototype. A possible explanation may be a high recombination rate between the CB and the IB, but we do not have clear evidences to affirm this.

The maximum voltage produced by the reference solar cell is 1.95 eV. This voltage surpasses the bandgap of the GaAs substrate divided by the charge of one electron (~ 1.5 V at 77 K [Levinshstein'99]). However, it still does not approach the ZnTe bandgap divided by the charge of one electron which is expected to be higher than 2.25 V at this low temperature. This may be explained by the presence of defects emerged from the large lattice-mismatch among the layers of the structures or may also be attributed to the band alignment of these hetero-structure solar cells. This will be analyzed in the following Section.

⁷ The theoretical J_{SC} for ideal ZnTe solar cell is 8 mA/cm² under AM1.5G spectrum [Smestad'08].

2.4.2 Performance limitations related to the hetero-structure of ZnTe solar cells

The solar cells studied in this Chapter are high bandgap solar cells grown on top of substrates of lower bandgap. The presence of this substrate can impose limitations in the solar cell performance. For example, if carrier mobilities were infinite, V_{OC} would be limited by the bandgap of the GaAs substrate (1.4 eV) and not by the bandgap of the ZnTe solar cell (2.25 eV) [Marti'13]. However, as can be seen in Fig. 2.17, at low temperature, the V_{OC} for the IBSC prototype and the reference solar cell is 1.8 V and 1.95 V, respectively. These values, multiplied by the electron charge, exceed the substrate bandgap, which is a proof that the fact carrier mobilities are finite impact the performance of the device. Thus, the only way of obtaining a V_{OC} higher than the bandgap of the substrate, at the same time that, in the substrate, photon stimulated emission does not overcome absorption processes, is to have a Fermi-level distribution as sketched in Fig. 2.18 (bottom). This Fermi-levels distribution was proposed in [Marti'13], where the spikes that appear in the bandgap diagram of hetero-structures were ignored for simplicity.

Fig. 2.18: (Top) Structure of a high bandgap solar cell grown on a substrate of lower bandgap. Under the hypothesis of infinite mobilities, quasi-Fermi level split cannot exceed the substrate bandgap (middle). Under the hypothesis of finite mobilities this split can overcome the substrate bandgap and approximate the p-n junction bandgap (bottom). The quasi-Fermi level split is equal to eV , where V is the output voltage of the solar cell (after [Marti'13]).

The band diagram of Fig. 2.18 (bottom) leads to ohmic losses related to carrier flow in the presence of a curvature of the quasi-Fermi levels [Luque'11a]. However, since

the gradient for each quasi-Fermi level becomes significant in regions in which these levels correspond to minority carriers, these ohmic losses might be not too high. A consequence of this band diagram is that increasing V_{OC} implies increasing ohmic losses, and consequently reducing J . This leads to a reduction of the FF.

In addition to the above mentioned, a low bandgap substrate can reduce the solar cells performance due to the fact that the rate at which carriers recombine increases as the bandgap is reduced⁸. Hence, the output voltage of solar cells on low bandgap substrates is expected to be lower than the output voltage of solar cells on high bandgap substrates. This is independent on where the carriers are generated, whether they are generated in the p-n junction or in the substrate. Usually, substrates are considered photovoltaic inactive, which means that in spite of carriers being generated in the substrate, they cannot be extracted to the external circuit. However the EQE measured in our solar cells shown that carriers generated in the substrates do contribute to the photocurrent. These solar cells have produced eV_{OC} higher than the photon energies absorbed in the substrate, which may be interpreted as electrons can be extracted at energies (eV_{OC}) higher than the energies used to generate them (the ones absorbed by the substrate). This interpretation contradicts the principles of thermodynamics and can be clarified by means of the analysis of our samples with the analytical model reported in [Martí'13]. We will use this model to simulate the QE and the $J - V$ characteristic of Fig. 2.12 and Fig. 2.17, considering a simple structure whose characteristics are listed in Table 2.I.

Table 2.I: Details of the structure modeled [Martí'13].

	p-ZnTe	n-ZnTe	n-GaAs
Thickness (μm)	1	1	1
Doping (cm^{-3})	10^{17}	10^{17}	10^{17}
Minority carrier diffusion constant (cm^2/s)	30	30	30
Minority carrier diffusion length(cm)	$4 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	15
Surface recombination (cm s^{-1})	0	-	0
Intrinsic concentration (cm^{-3})	10^{-1}	10^{-1}	10^6
Absorption coefficient	[Ullah'14]	[Ullah'14]	[Martí'92]
Intrinsic level	mid-gap	mid-gap	mid-gap

⁸ The total recombination rate is determined by the dark saturation current density which is proportional to the square of the intrinsic concentration, n_i^2 and therefore to $\exp\left(\frac{-E_G}{2k_B T}\right)$ [Pierret'87].

Fig. 2.19: Simulated quantum efficiency for ZnTe solar cell on GaAs substrate (a) and its corresponding current density – voltage characteristic under different illuminations. In (b), an illumination with 6000 K black body radiation has been assumed under a solar concentration of 1000 suns. In this case, the current density is expressed as current per unit of concentrator area. In (c), a monochromatic illumination with 1.5 eV photons is assumed. The illumination power used in this case ($40 \mu\text{W}$) is the maximum value so that the quasi-Fermi level split keeps within the bandgap boundaries. In (a) and (b) experimental results are plotted to facilitate the comparison.

The simulations presented in Fig. 2.19 basically reproduce the experimental results. On one hand, the simulated QE shows values of the same order of magnitude as the experimental results of Fig. 2.12. The experimental EQE for photon energies close to the value of the GaAs bandgap was around 10^{-4} and it was around 0.16 for photon energies close to the ZnTe bandgap, which agrees with the simulations of Fig. 2.19 (a). On the other hand, the simulated V_{OC} obtained under concentrated white-light in Fig. 2.19 (b) matches with the V_{OC} obtained experimentally at low temperature in Fig. 2.17 (bottom). This V_{OC} is close to 2 eV and it is not limited by the GaAs bandgap because most photons are absorbed in the ZnTe p-n junction (according to the QE) when the cell is illuminated with polychromatic spectrum. Furthermore, the eV_{OC} cannot exceed the value of the GaAs bandgap when photons can only be absorbed in the substrate. This is illustrated in Fig. 2.19 (c), where the cell is illuminated with 1.5 eV photons. This result indicates that electrons cannot be extracted at a higher voltage than the energy of the photons used to generate them divided by the charge of one electron.

In both curves, the simulated and the experimental $J - V$ characteristics, eV_{OC} never approaches the value of ZnTe bandgap. The reason may be that the band lineup of the structure leads to a built-in potential lower than the ZnTe bandgap. To evidence this limitation, in Fig. 2.20 we plot the theoretical built-in potential and ZnTe bandgap energy together with the experimental V_{OC} produced by the reference solar cell R1024 under high irradiances and different temperatures [Teran'15].

Fig. 2.20: Temperature dependence for: the measured V_{OC} for the reference solar cell R1024 under solar concentration (black squares), the calculated built-in potential (dashed red line) and the calculated ZnTe bandgap (dotted line blue). The plot is reprinted from [Teran'15], where the temperature dependence of the built-in potential and ZnTe bandgap is calculated using the Varshni parameters from [Pässler'99] and the electron affinities for ZnTe and ZnSe from [Kasap'07].

Fig. 2.20 indicates that in our solar cells the V_{OC} is limited by a built-in potential lower than the ZnTe bandgap. These results underscore the importance of identifying hetero-junctions with desirable energy band lineups, where low-defect density may also be achieved.

2.5 Summary

In collaboration with the University of Michigan we have characterized IB materials and IBSC prototypes based on ZnTe:O HMAs grown by MBE. We have demonstrated the presence of both sub-bandgap optical transitions ($VB \rightarrow IB$ and $IB \rightarrow CB$) in ZnTe:O materials by means of reflectance spectra measurements, PL measurements and absorption measurements. The experimental results have evidenced a bandgap distribution characterized by $E_L = 0.4$ eV, $E_H = 1.85$ eV and $E_G = 2.25$ eV. The absorption coefficient related to the $VB \rightarrow IB$ transition has been estimated to be around 10^4 cm^{-1} , which is in agreement with previous works [Tooru'11]. For the first time, the $IB \rightarrow CB$ transition has been spectrally resolved in these materials by means of the measurement of its absorption coefficient. This absorption coefficient has shown a maximum value of 750 cm^{-1} at 0.4 eV, and a strong selective character that only allows photons with energies in the 0.3-0.5 eV range to be absorbed in the $IB \rightarrow CB$ transition. This strong selective

character is a distinctive signature of transitions between localized states, and suggests that the intermediate states (denoted as IB) do not form an actual energy band in the samples studied. The hypothesis we have considered to explain this possibility is that an insufficient concentration of O_{Te} was present in the lattice of the ZnTe:O materials. This hypothesis is supported by the BAC model, which predicts that the energy band distribution of the ZnTe material corresponds to a low O molar composition (Section 2.3). Previous SIMS measurements revealed that the samples studied contain an O concentration of around 10^{19} cm^{-3} . On one hand, this concentration is lower than the concentrations explored in theoretical works, where the formation of an IB was predicted [Tablero'10]. On the other hand, O concentration is not the same than O_{Te} concentration when, for example, oxygen pairs or oxygen clusters are formed. These reasons could explain the insufficient low O_{Te} concentration. Either way, we consider that O_{Te} concentration should be increased not only to form a real IB, but also to obtain a more optimum bandgap distribution, through a blue-shift of the E_L .

The IBSC operation principles have not been proven in the IBSC prototypes studied in this Chapter. Photocurrent measurements have not evidenced the generation of two-photon photocurrent, in spite of having tried to increase the rate of optical sub-bandgap transitions by photo-filling the IB and suppressing non-optical mechanisms that compete with it. This could be due to the low value of the absorption coefficient related to IB→CB transitions and its strong selective character. If this were the case, the detection of two-photon photocurrent may require the use of high irradiances of 0.3-0.5 eV photons. Another possibility for not detecting two-photon photocurrent could be the presence of a high de-excitation rate between the CB and the IB. Unfortunately, this could not be tested due to the practical limitations of our experimental set-ups.

From the measurements of the current-voltage characteristics, we have not been able to discard the possibility that the intermediate states limit the output voltages of the cells. Since the output voltage produced by the IBSC prototypes studied in this Chapter have not surpassed E_H/e , although we have tried to maximize its value by using concentrated white-light and low temperatures. This could be due to the low absorption coefficient related to the IB→CB transitions, the presence of high de-excitation rates between the CB and the IB, or a combination of both. Also, we have seen that the structural characteristics of the solar cells make it difficult to demonstrate the voltage preservation principle because they lead to a reduction of the output voltage. On one hand, the V_{OC} is limited by a built-in potential lower than the ZnTe bandgap. On the other hand, the use of low bandgap substrates such as GaAs increases the recombination rates and also reduces the V_{OC} . For these reasons, we consider it necessary to fabricate ZnTe homo-junction solar cells grown on the top of ZnTe substrates through the growth of high quality n-type ZnTe. These devices not only would facilitate the demonstration of the voltage preservation

principle (if this were the case), but could also lead to better crystal qualities and better performances of the solar cells.

3 RESEARCH IN IBSC BASED ON DEEP-LEVEL IMPURITIES

3.1 Introduction

One of the technological approaches proposed to fabricate IB materials consists of introducing impurities of a specific element inside the lattice of a specific host semiconductor, at a high concentration [Luque'06a]. The presence of these impurities can lead to the emergence of deep-levels (DLs) inside the bandgap of the semiconductor, from which an IB can be formed. Several works have suggested some impurity-host semiconductor combinations suitable to form an IB, for example, materials based on incorporating transition metals into conventional bulk semiconductors [Wahnon'02]. However, the low solubility of transition metals in semiconductors can make their incorporation difficult at a high concentration. As mentioned in Section 1.2.2, this concentration must surpass the Luque limit, whose value depends on the impurity-host semiconductor combination and is around $\sim 10^{20} \text{cm}^{-3}$ [Luque'06a]. Perhaps, this difficulty is one of the reasons why, in some cases, these materials have been the least investigated to implement IBSCs in comparison with QDs and HMAs. In this Chapter we will try to contribute to the research on this kind of materials by studying the particular case of IBSCs based on Si:Ti and GaAs:Ti.

In Section 1.2.2 we mentioned that one way to inhibit the non-radiative recombination (NRR) associated to DLs consists of de-localizing the wave function of these states [Luque'06a]. In that Section, we did not discuss the nature of the NRR. We limited ourselves to justifying that the de-localization of DL states can lead radiative transitions dominating over recombination processes, which can be understood as an

inhibition of NRR. In this Section we will analyze the NRR inhibition from another perspective, focusing on the nature of the NRR associated to DLs. The mechanisms associated to this NRR are discussed in detailed in [Lang'75;Luque'06a]. The analysis of the NRR will allow us to understand why some authors reject the NRR inhibition predicted by the IB theory [Krich'12].

The physical mechanism that dominates NRR in bulk semiconductors can vary from case to case [Queisser'78]. In general, it has been accepted that the NRR associated to DLs can be dominated by phonon emission, which are vibration modes of the lattice with energies is in the 0.01-0.03 eV range. These energies are lower than the energetic jump that is produced in the NRR (around 1-2 eV), which makes it necessary for several phonons to be emitted during the NRR. This emission is explained in [Lang'75] using the model known as multi-phonon emission (MPE). This model establishes that the vibration modes of the lattice modulate the position of DLs inside the bandgap [Lang'75;Luque'06a], as depicted in Fig. 3.1 (a). In this figure the position of DLs respect to the VB and the CB are represented by E_p and E_n respectively, for different generalized lattice coordinates (Q). The configuration diagram of Fig. 3.1 (b) represents the potential energy of electrons in the CB (U_C), in the VB (U_V) and in one DL introduced by one impurity (U_t). The horizontal lines correspond to the total energy determined by the potential energy plus the nuclei kinetic energy. According to this diagram, the non-radiative recombination of an electron is produced by the following process. Prior to capture, the equilibrium position of the DL is in the upper half of the gap ($Q = 0$). For sufficiently large vibrations, which become more probable as temperature increases, the unoccupied DL state can cross into the CB and capture an electron (Q_C). In this process, the electrical transition is produced from a de-localized state to a localized one. This transition causes an important movement of the charge distribution, since, initially, the electron is distributed among many atoms and, afterwards, it is localized next to the impurity atom. The re-distribution of the charge changes the equilibrium position of the impurity, which vibrates violently in real space in a mode other than the usual lattice phonons, the so-called breathing mode. This breathing mode is attenuated through the successive emission of phonons, produced by conventional electron-phonon interaction, until the occupied DL state crosses into the VB (Q_V) and transfers the electron to this band.

Fig. 3.1: (a) Electronic energy versus lattice coordinates, Q . (b) The configuration-coordinate diagram for the case of one impurity that introduce one DL state inside the bandgap of the semiconductor (after [Lang'75]).

According to [Luque'06a], if impurities are introduced at a concentration above the Luque limit, the wave function of the DLs associated to impurities becomes de-localized. In this case, the recombination through DLs does not imply charge localization, nor the appearance of breathing modes. Therefore, under these circumstances, the MPE associated to NRR can be inhibited and the collection of DLs can behave as an IB. Experimentally, the NRR inhibition can be demonstrated by proving that a sufficiently high concentration of impurities can cause the recovery of the carrier lifetime. This demonstration was reported in IB materials based on Si:Ti [Antolin'09].

In [Krich'12], the authors extended the MPE theory to a situation of many impurity atoms. In that work the authors conclude that, even when the impurity concentration is high enough to de-localize the IB-states in the equilibrium position ($Q = 0$), lattice vibrations can raise an IB state above the CB minimum. In this situation the electron-phonon interaction determines the wave function of the IB state, which can become sufficiently localized (Q_c) to cause recombination by MPE. This is illustrated in Fig. 3.2. According to this argument, the NRR recombination cannot be suppressed by means of the increase in impurity concentration. However, a lifetime recovery can be obtained if the increase in the impurity concentration leads to a perturbation that moves IB energy levels uniformly away from the centre of the bandgap. The difference of this lifetime recovery with respect to the one predicted by the IB theory, is that this one is not associated to the formation of an IB and is not useful for IBSC implementation. In spite of these negative predictions, in [Krich'12] the authors maintain that IBSCs based on DLs still have

potential to be highly efficient solar cells if they are fabricated with materials with strong absorptivity, capable of compensating the NRR.

Fig. 3.2: Sketch of a crystal of gray spherical atoms with blue diamond impurities. In this sketch the light green represent the wave function of an IB-state. a) In the equilibrium position ($Q=0$), the proximity between impurity atoms lead to delocalized IB-states with energies in the $\epsilon_1 - \epsilon_2$ range. b) lattice distortion moves the atoms surrounding an impurity away from their equilibrium positions. For sufficiently large deviations of the host atoms, electron-phonon interaction determines the IB-state. This state becomes localized at that impurity and its energy approaches the energy of the CB. If this IB-state crosses the CB a rapid trapping will occur. (after [Krich'12])

3.2 IBSC based on silicon

Silicon (Si) is a widely studied semiconductor. That is why it is interesting to use this semiconductor as a workhorse to develop IBSCs, in spite of its bandgap (~ 1.12 eV) being quite far from the optimum value (1.95 eV). Besides, Si is the most abundant element of the Earth crust after oxygen (27.7% by weight [Suess'56]) and it is the most used semiconductor in photovoltaic industry. For this reason, even a modest efficiency gain resulted from creating an IB within the Si bandgap could trigger a large commercial interest, if the IB is created at a low cost.

The efficiency of a Si-IBSC depends on the absorption coefficients of this device, α_{VC} , α_{VI} and α_{IC} , which, unfortunately, are unknown. In general, absorption coefficients of IBSCs can be classified as selective or non-selective. The value of selective absorption coefficients do not overlap at any photon energy, while the value of non-selective absorption coefficients overlap for some photon energies. In [Luque'97a], selective absorption coefficients were considered to determine the limit efficiency of IBSCs, because this kind of coefficients minimalizes the energy lost by thermalization processes (illustrated in Fig. 3.3). In another work [Cuadra'04b], the influence of non-selective absorption coefficients on the efficiency of IBSCs was studied. In that work, a laborious mathematical model was used to conclude that an arbitrary overlap between the three absorption coefficients reduces the limiting efficiency of IBSCs and makes the thickness of the IBSC a parameter that needs to be optimized. In this Section we will use the mathematical model described in [Cuadra'04b] to compare the limiting efficiency of Si-IBSCs with selective and non-selective absorption coefficients.

Fig. 3.3: Illustration of the energy lost by electrons through thermalization processes (E_{loss}) in the case of selective (left) and non selective (right) absorption coefficients.

The model is based on the detailed balance and assumes that the sun and the surroundings are black bodies at 6000 K and 300 K respectively, and the IBSC is a body at 300 K. According to the model, the $J - V$ characteristic is given by:

$$J(V) = e \int_E M_e (F_{abs} - F_{em}) dE - J_{B,e} = e \int_E M_h (F_{abs} - F_{em}) dE - J_{B,h} \quad (3.1)$$

where E is the photon energy and

$$M_e = \frac{\alpha_{VC} + \alpha_{IC}}{\alpha_{VC} + \alpha_{IC} + \alpha_{VI}} \quad (3.2)$$

$$M_h = \frac{\alpha_{VC} + \alpha_{VI}}{\alpha_{VC} + \alpha_{IC} + \alpha_{VI}} \quad (3.3)$$

F_{abs} is the photon flux absorbed by the IBSC and F_{em} is the photon flux emitted by the IBSC. $J_{B,e}$ and $J_{B,h}$ are loss factors associated to photon recycling processes that cause the re-absorption of photons in transitions with an energy threshold lower than those in which they were created.

As explained in [Cuadra'04b], the loss factors $J_{B,e}$ and $J_{B,h}$ depend on the cell thickness. These loss factors can be made arbitrarily small if the cell thickness tends to zero, so a priori, the most efficient Si-IBSCs are those thin enough so as to consider $J_{B,e} = J_{B,h} = 0$. In thin solar cells the use of light trapping techniques is required to enhance the optical absorption [Campbell'86;Yablonovitch'82]. Therefore, theoretical Si-IBSCs with $J_{B,e} = J_{B,h} = 0$ and absorptivity equal to 1 correspond to practical Si-IBSCs with minimum thicknesses and elements for trapping light. These theoretical IBSCs are those studied in this Section. To simplify the study we assume that there can be overlapping between the absorption coefficients α_{IC} and α_{IV} , but not with α_{VC} . This hypothesis can be considered as an approximation describing the case where photons capable of causing transitions from the VB to the CB are absorbed in the front emitter of the cell. The task of dealing with the absorption of photon energies below the bandgap value correspond to the IB material. Under these considerations, M_e and M_h are given by:

$$M_e = \begin{cases} 1 & \text{if } E_L < E < E_H \\ \frac{\alpha_{IC}}{\alpha_{IC} + \alpha_{VI}} = \gamma & \text{if } E_H < E < E_G \\ 1 & \text{if } E > E_G \end{cases} \quad (3.4)$$

$$M_h = \begin{cases} 1 & \text{if } E_L < E < E_H \\ \frac{\alpha_{VI}}{\alpha_{IC} + \alpha_{VI}} = 1 - \gamma & \text{if } E_H < E < E_G \\ 1 & \text{if } E > E_G \end{cases} \quad (3.5)$$

Under the considerations mentioned above we can obtain the $J - V$ characteristic for Si- IBSCs by using equation (1.4) and replacing $\dot{N}$ by $M_e \dot{N}$, or by using equation (1.5) and replacing $\dot{N}$ by $M_h \dot{N}$. Once the $J - V$ characteristic has been determined, the maximum power point and, therefore, the efficiency of the cell can be calculated. These data can be obtained for different E_L , whose value is swept from zero to the value of half the Si bandgap, since the results are symmetric with respect to the mid-gap. The results obtained with this procedure are plotted in Fig. 3.4, where several solar concentrations are considered, 1 sun (a), 100 suns (b) and maximum concentration, 46050 suns (c). In this figure the curves labelled as NOV correspond to the case in which absorption coefficients α_{IC} and α_{IV} do not overlap and the curves labelled as OV correspond to the case in which these absorption coefficients do overlap. In the OV case, for each E_L , the degree of overlap (γ) is optimized for maximum efficiency.

(a)

(b)

Fig. 3.4: Limiting efficiency for Si conventional solar cells and Si-IBSCs, whose IB is located at different positions within the Si bandgap. The acronym NOV means that the absorption coefficients α_{IC} and α_{IV} do not overlap and the acronym OV means that the absorption coefficients do overlap. Three different sunlight concentrations have been assumed for the calculus: (a) 1 sun, (b) 100 suns and (c) 46050 suns. (after [López'14])

Fig. 3.4 shows that the limiting efficiency of Si-IBSCs and Si conventional solar cells are equal for $E_L/E_G = 0$, since this point corresponds to the case where there is no IB. These limiting efficiencies are also equal for an IB located at the mid-gap ($E_L/E_G = 0.5$) if absorption coefficients do not overlap (NOV). This is because in this latter case the IB does not contribute at all to the enhancement of the photocurrent, neither to the radiative recombination.

Under one-sun illumination (Fig. 3.4a), the limiting efficiency of Si-IBSCs is lower than the limit efficiency of Si conventional solar cells, for any position of the IB with the exceptions of the particular cases mentioned above. These results evidence that, at one sun, there is no efficiency advantage of using Si-IBSC over conventional silicon cells. The situation changes when concentrated sunlight is used to illuminate the solar cell. Under these illumination conditions, the limiting efficiency of a Si-IBSC is higher than the limiting efficiency of a Si conventional solar cell, as shown in Fig. 3.4 (b) and (c). These results make it evident that implementation of Si-IBSCs will only make sense if concentrated sunlight is used in these devices. In particular, an efficiency as high as 54.6% can be achieved by a Si-IBSC, assuming maximum sunlight concentration, selective absorption coefficients and optimal bandgaps ($E_L/E_G = 0.32$). For E_L/E_G above 0.32, non-selective absorption coefficients (with $0 \leq \gamma \leq 0.5$) can lead to higher efficiencies than those provided by selective coefficients. This result, emphasized for the first time in [López'14], attracts our attention since it seems to contradict what is conventionally assumed.

Selective coefficients have usually been considered as the most appropriate ones to maximize efficiency, since these coefficients minimize thermalization processes. However, if we deal with non-optimum bandgaps, non-selective absorption coefficients can provide higher efficiencies due to a better match between sub-bandgap transitions $VB \rightarrow IB$ and $IB \rightarrow CB$. Therefore, the condition that these absorption coefficients should not overlap, required for attaining the IBSC with the absolute maximum efficiency, should not be pursued in research where non ideal bandgaps are used.

3.2.1 Experimental results in IBSCs based on Si:Ti

In spite of it being well-known that Ti is a lifetime killer for carriers in Si [Rohatgi'80], IBSCs based on the incorporation of large amounts of Ti in c-Si was experimentally studied, for the first time, in [Olea'08]. In that work it was suggested that, in Si:Ti, an IB may be created at 0.21 eV from the CB when the Ti concentration is above the Luque limit. This was supported by *ab initio* calculations reported in [Sánchez'09], where it was concluded that Ti interstitial atoms in a Si host lattice may lead to the formation of an IB, which may receive one to four electrons from each Ti atom. Theoretical and experimental results have revealed that interstitial Ti atoms configure the most stable Si:Ti material [Pastor'12;Sánchez'09].

One way to obtain crystalline Si (c-Si) with a Ti doping above Luque limit consists of using ion implantation to introduce Ti atoms inside c-Si lattice. This procedure can damage the crystal quality of the layer implanted. For this reason implantation processes are usually accompanied by annealing processes, which facilitate the recovery of the crystal structure. However, since the reported solubility for Ti in Si is much lower than the Luque limit [Hocine'88;Mathiot'91], conventional annealing methods should be avoided to prevent the formation of Ti clusters. Instead, methods capable of avoiding equilibrium constraints need to be applied, such as pulsed laser melting (PLM). In this technique, the implanted surface is irradiated with a high energy laser pulse to melt the damaged layer for an interval of several nanoseconds and let it re-crystallize using the underlying material as a seed. The combination of implantation and PLM techniques can provide wafers of c-Si with an implanted Ti depth profile similar to the one depicted in Fig. 3.5.

Fig. 3.5: Ti depth profile obtained from SIMS measurements. This profile is the result of implanting Ti atoms in the crystal direction [111] of a c-Si wafer with an energy of 35 keV and a dose of 10^{16}cm^{-2} Ti atoms, with subsequent PLM annealing of 1.4 J/cm^2 (Courtesy of Dr. David Pastor).

From Fig. 3.5 it can be seen that the most superficial region of c-Si wafers implanted with Ti (approximately the first 80 nm in this case) may contain a Ti concentration above the Luque limit. According to [Luque'06a;Sánchez'09], if all Ti atoms, or at least 10% of them, occupy interstitial positions, the NRR produced through DLs associated to Ti atoms can be inhibited in the superficial region. This fact is supported by the results reported in [Antolín'09], where a recovery of the carrier lifetimes is demonstrated by increasing the Ti concentration above the Luque limit. However, in spite of this recovery, in [Antolín'09] the value of the carrier lifetimes did not recover to the level shown in c-Si wafers without Ti. This may be due to the presence of regions with Ti concentrations below the Luque limit, where the DLs act as a source of high NRR. The unavoidable presence of Ti tails in implanted samples can constitute a drawback for the fabrication of IB materials with this technique.

The first IBSC prototypes based on Si:Ti have been fabricated thanks to the collaboration between the Universidad Complutense de Madrid (UCM) and the Universidad Politcnica de Catalua (UPC) [Silvestre'13]. These devices are obtained after several manufacturing steps:

- (1) Fabrication of IB materials based on p-type c-Si wafers implanted with Ti at the UCM. In this process a VARIAN CF3000 Ion Implanter refurbished by Ion Beam Services is used. The energy range and the dose range during the implantation are 35-150 keV and $10^{15} - 10^{16}\text{cm}^{-2}$ respectively.
- (2) PLM annealing of the implanted wafers performed by J.P. Sercel Associates Inc. (New Hampshire, USA). The energy density applied during the annealing process is of 1.4-1.8 J/cm², using 20 ns long pulse of a KrF excimer laser (248nm).

- (3) Fabrication of n-emitters based on hydrogenated amorphous Si (a-Si:H) and back surface field layers based on a-SiCx:H at the UPC. These layers are fabricated using plasma enhanced chemical vapor deposition (PECVD).
- (4) Deposition of anti-reflection coatings of ITO and the top and bottom metal contacts at the UPC. These layers are deposited using a RF magnetron sputtering, sputtering and thermal evaporation respectively.

In order to prevent the degradation of the Ti-supersaturated layer of the IBSC prototypes, all processes described above are conducted at low temperatures ($T < 200\text{ }^{\circ}\text{C}$). The implanted surface of the c-Si wafer is passivated by depositing an intrinsic a-Si:H layer on it, leading to solar cells with the HIT structure of Fig. 3.6 [Makoto'92]. HIT solar cells with and without Ti-implantation (the latter as reference solar cells) have been characterized at the IES-UPM to test whether this technology is able to provide functional IBSCs.

Fig. 3.6: Structure of HIT solar cells (Courtesy of Dr. Santiago Silvestre).

In Section 3.2 it was mentioned that Si-IBSCs can be more efficient than conventional Si solar cells under concentrated sunlight. To test this we have taken $J - V$ measurements under high irradiance conditions, following the technique described in Section 2.3.3. The $J - V$ characteristics of two representative cells, one HIT reference cell without Ti and one HIT-IBSC prototype with Ti, are shown in Fig. 3.7.

Fig. 3.7: $J - V$ characteristics at room temperature of the reference solar cell (black circles) and the IBSC prototype (red circles). The curves are obtained by illuminating the solar cells with the concentrated light of a Xenon flash. To induce high output voltages the $J - V$ characteristics are also measured at 77 K (squares).

The $J - V$ characteristics of Fig. 3.7 were obtained under nominally identical illumination spectrums. These curves evidence a poor performance of the solar cells, especially in the case of the HIT-IBSC prototype. These poor performances are related to the presence of non-ideal elements, such as high series resistances and low shunt resistances, which strongly impact the $J - V$ characteristics of the solar cells. Due to the presence of shunt resistances, J_L cannot be extracted from the $J - V$ characteristics. As a consequence, the irradiance level used to illuminate the samples cannot be determined, neither can J/X and η values. One parameter that can be clearly extracted from these curves is the V_{OC} of the cells. Experimentally, it has been observed that eV_{OC} can approach E_G when solar cells operate under concentrated sunlight [García-Linares'12]. However, the maximum eV_{OC} obtained by the reference solar cell under high irradiances is 0.72 eV at room temperature and 0.82 eV at 77 K, which is far from the c-Si bandgap $E_G = 1.12$ eV. The reason for this may be that the built-in voltage of the solar cells is lower than 1.12 V due to the low doping level of the p-type c-Si, which is around $9 \cdot 10^{15} - 6 \cdot 10^{16} \text{ cm}^{-3}$. The V_{OC} obtained by the IBSC prototype under high irradiances recovers from 0.39 V at room temperature up to 0.52 at 77K, which is a remarkable increase, but still far from the V_{OC} obtained by the reference solar cell. To understand why the V_{OC} of the HIT-IBSC prototype is significantly lower than the V_{OC} of the reference solar cell, additional experimental results are shown below in this Section.

The dark $J - V$ curves can give information about the recombination processes present in solar cells. As explained in [García-Linares'13a], the interpretation of these curves can be affected by the effects of series resistances. These effects are usually

detected at high current values, producing a bending of the curves towards high voltages. In order to eliminate the impact of series resistances, in [García-Linares'13a] the authors propose the measurement of $J_L - V_{OC}$ pairs at different irradiance levels. In conventional solar cells, these $J_L - V_{OC}$ curves may reproduce the dark $J - V$ curves, except for the part of the curve affected by series resistance. The concordance between $J_L - V_{OC}$ and dark $J - V$ curves is known as the superposition principle. This principle should be fulfilled in conventional solar cells whether the recombination under dark conditions and under illumination conditions are dominated by the same mechanisms. Simulations obtained with the detailed balance and some experimental results indicate that, in IBSCs, the $J_L - V_{OC}$ curves can accurately match the dark $J - V$ curves in those parts not affected by series resistances [García-Linares'12].

As mentioned previously, in the reference solar cell and the IBSC prototype J_L cannot be obtained. For this reason, in these solar cells, instead of measuring $J_L - V_{OC}$ curves, we measure $J_{SC} - V_{OC}$ curves using the technique described in Section 2.3.3. Fig. 3.8 shows the results obtained for the reference solar cell (a) and the HIT-IBSC prototype (b) at room temperature (~ 295 K) and at 77 K, together with the dark $J - V$ curves. While in the reference solar cell, the $J_{SC} - V_{OC}$ curves match the dark $J - V$ curves at low current ranges, where the effects of the series are not significant, in the IBSC this does not occur at 77 K. Maybe the reason is that, at 77 K, the mechanisms that dominate the recombination under dark conditions are different to the mechanisms that dominate the recombination under illumination conditions. However, for the moment, it is not clear that IBSCs should fulfill the superposition principle, so we cannot extract any conclusion from the mismatch between the curves of the IBSC prototype at 77 K.

Fig. 3.8: (c) Dark $J - V$ curves (solid lines) of the reference solar cell (black color) and the HIT-IBSC prototype (red color) at room temperature ($\sim 295\text{ K}$) and 77 K . In (a) and (b) these curves are plotted together with the $J_{\text{SC}} - V_{\text{OC}}$ curves (cross points) of the reference solar cell and the HIT-IBSC prototype respectively. Each point of $J_{\text{SC}} - V_{\text{OC}}$ curves is obtained under different irradiance levels resulting from the discharge of a Xenon flash.

At room temperature ($\sim 295\text{ K}$), the dark current density of the HIT-IBSC prototype is higher than the dark current density of the reference solar cell at every voltage value (Fig. 3.8c). According to [Martí'06b], this fact indicates that the recombination processes in the IBSC prototype are stronger than in the reference solar cell. This stronger recombination can explain why, at room temperature, the maximum V_{OC} obtained with the HIT-IBSC prototype (0.39 V in Fig. 3.8b) is significantly lower than the maximum V_{OC} obtained with the reference solar cell (0.72 V Fig. 3.8a). This hypothesis

is also supported by the fact that, at room temperature, the maximum J_{SC} obtained with the IBSC prototype ($845 \text{ mA} \cdot \text{cm}^{-2}$ in Fig. 3.8b) is lower than the maximum J_{SC} obtained with the reference solar cell ($2500 \text{ mA} \cdot \text{cm}^{-2}$ in Fig. 3.8a). There is another explanation compatible with these results that consists in, maybe, that the irradiance that illuminates the IBSC prototype is lower than the irradiance that illuminates the reference solar cell. This is possible since in spite of our great care, we are not able to assure that both solar cells are measured under the same illumination conditions. However, this second explanation can be discarded in view of the results obtained at 77 K. At 77 K, the maximum J_{SC} obtained with the IBSC prototype ($855 \text{ mA} \cdot \text{cm}^{-2}$ in Fig. 3.8b) is higher than the maximum J_{SC} obtained with the reference solar cell ($321 \text{ mA} \cdot \text{cm}^{-2}$ in Fig. 3.8a).

At 77 K, the maximum V_{OC} obtained with the HIT-IBSC prototype (0.52 V in Fig. 3.8b) is again significantly lower than the maximum V_{OC} obtained with the reference solar cell (0.83 V in Fig. 3.8a). However, in this case, we cannot justify the lower V_{OC} of the IBSC with a stronger recombination because, at 77 K, the dark current density of the HIT-IBSC prototype is significantly lower than the dark current density of the reference solar cell (Fig. 3.8c). According to this fact, there should be another explanation that justifies why at 77 K, the V_{OC} of the IBSC prototype is limited to ~ 0.5 V. This limitation should be related to the Ti-implantation of the IBSC prototype, since this is the only significant difference between the two types of solar cells studied here. We advance that this limitation is due to a reduction of the effective bandgap of the HIT-IBSC prototype, consequence of tunneling transfer between the IB and the CB (see below).

In order to determine whether the V_{OC} of the HIT-IBSC prototype is limited by the presence of an IB, it is necessary to compare eV_{OC} with the value of the two sub-bandgaps E_H and E_L . Previous works have obtained the value of these sub-bandgaps from the absorption threshold provided by spectral response measurements [Ramiro'14a]. We will follow the same approach to determine E_H and E_L , by measuring the EQE of the solar cells studied in this Section (Fig. 3.9).

Fig. 3.9: EQE of a reference solar cell (solid black line) and two HIT-IBSC prototypes. In one of the two prototypes the intrinsic layer has a thickness of 5 nm (solid red line). The other prototype has a thicker intrinsic layer of 20 nm (dashed red line). The results are obtained at room temperature by illuminating the samples with the monochromatic light from the output of a 1/4 m monochromator. IBSC prototypes show spectral response at energies below the bandgap. The inset shows the supra-bandgap EQE in a lineal scale.

Fig. 3.9 shows the EQE of the reference solar cell (solid black line) and the HIT-IBSC prototype (solid red line). This figure evidences that, for photon energies higher than the c-Si bandgap (~ 1.12 eV), the EQE of the reference solar cell is higher than the EQE of the HIT-IBSC prototype. The reason may be a carrier lifetime reduction in the Si:Ti material. This reduction may be related to the tails of Ti atoms, which act as lifetime-killers when their concentration is below the Luque limit. This argument is in agreement with $J - V$ characteristics obtained at room temperature (Fig. 3.8).

Fig. 3.9 also evidences a sub-bandgap response in the HIT-IBSC prototype, from 0.75 eV to 1 eV, which is not present in the reference cell. This fact suggests that the sub-bandgap response is related to DLs introduced during the Ti-implantation process. Hereinafter, we will refer to these DLs as IB, without distinguishing between DLs associated with Ti atoms and DLs associated with defects introduced during the implantation process. The sub-bandgap EQE of the HIT-IBSC prototype is quite low, around 0.01%. This can induce us to believe that the absorption coefficients associated to sub-bandgap transitions are not strong enough for PV applications. However, in [Olea'11a], an absorption coefficient of 10^4 cm^{-1} was reported for sub-bandgap transitions in Si:Ti. This absorption threshold is high enough to allow 90% of the incident sub-bandgap photons to be absorbed in a thickness of $2 \mu\text{m}$. Therefore, the reason why the sub-bandgap EQE of the HIT-IBSC prototype is so low may be because the implanted Ti-layer is so thin, at around 150 nm according to SIMS measurements. A thicker Ti-layer is

recommendable to achieve significant improvements in the sub-bandgap EQE of HIT-IBSC prototypes.

The sub-bandgap response of the HIT-IBSC prototype is the result of pumping electrons from the VB to the CB. Since this pumping process is produced by illuminating the HIT-IBSC prototype with photon energies below the Si bandgap ($\sim 1.12\text{eV}$), the mechanism involved must differ from conventional VB $\rightarrow$ CB optical transitions. This mechanism may consist in two pumping processes in which sub-bandgap photons excite electrons from VB to IB and from IB to CB. Another possibility could be that one of these two sub-bandgap transitions, probably the transition IB $\rightarrow$ CB, is produced by thermal generation and/or tunnel transport mechanisms, which do not produce electrical work [Luque'01;Luque'02]. In either case, the absorption threshold of the EQE of the HIT-IBSC prototype ($\sim 0.75\text{eV}$) should correspond to the value of the sub-bandgap E_H . This fact suggests a bandgaps distribution formed by $E_G \approx 1.12\text{eV}$, $E_H \sim 0.75\text{eV}$ and $E_L \sim 0.37\text{eV}$, which agrees with that reported in [Olea'11b]. The maximum V_{OC} obtained by the HIT-IBSC prototype (0.52 V) exceeds the sub-bandgap E_L (0.37 eV) but not the sub-bandgap E_H (0.75 eV). In view of these results, the voltage preservation principle is not demonstrated in the HIT-IBSC prototype.

According to the band diagram of the HIT-IBSC prototype (Fig. 3.10 top), the 5nm of the intrinsic a-Si:H layer (Fig. 3.6) is the separation between the IB and the CB of the n-emitter (n-type a-Si:H). This minimal separation facilitates the escape of carriers from the IB to the CB by tunnel mechanisms. To reduce the intensity of possible tunnel-effects, we have characterized HIT-IBSC prototypes with a thicker intrinsic a-Si:H layer (20 nm), which lead to a better isolation of the IB (Fig. 3.10 bottom). The EQE of one of these HIT-IBSC prototypes is represented by the dashed red line in Fig. 3.9.

Fig. 3.10: Simulated band diagram of the hetero-structure: n-type a-Si:H/ intrinsic a-Si:H/IB c-Si. Two cases are represented, the case in which the thickness of the intrinsic layer is 5nm (top) and the case in which this thickness is 20 nm (bottom). Processes of thermal generation and tunnel transport are illustrated by black arrows. The latter one can be assisted by the presence of defect levels in the intrinsic a-Si:H layer (after [Silvestre'13]).

The results seen in Fig. 3.9 indicate that the EQE of the “20nm prototype” is higher at energies above 1 eV (as shown in the inset of the figure) and lower at sub-bandgap energies from 0.75 eV to 1 eV, when compared to the EQE of the “5nm prototype”. The reduction in the sub-bandgap response obtained by increasing the thickness of the intrinsic layer can be justified by a tunnel-connection between the IB and the CB of the n-type a-Si layer [Silvestre'13]. The presence of this mechanism is in agreement with $J - V$ characteristics obtained at 77 K (Fig. 3.8) and justifies why the voltage preservation principle is not demonstrated in HIT-IBSC prototypes.

3.3 IBSC based on GaAs

GaAs is one of the most studied III-V semiconductors, with a large body of investigation in PV applications [Green'15]. The maturity of GaAs technology is useful to manufacture efficient solar cells [Green'15] and allows us to know the energy levels introduced inside the GaAs bandgap by different transition metals [Hennel'93]. For these reasons, choosing this material to implement IBSC based on DLs can be advantageous. Besides, while the GaAs bandgap (~ 1.42 eV) is not optimum, it can still lead to IBSCs with reasonable efficiencies. Fig. 3.11 shows the limiting efficiency of GaAs-IBSCs calculated in [Martí'09] using the detailed balance model. In this figure, empty dots indicate that the IB

of the GaAs-IBSC is located at the same positions as the DLs introduced inside the GaAs bandgap by different transition elements: Co, Ti, Ni, Fe, Cr, V and Mn [Hennel'93].

Fig. 3.11: Limiting efficiency of GaAs-IBSCs as a function of the IB position. The empty dots indicate that the IB is located at the same positions as the DLs introduced inside the GaAs bandgap by different transition elements. The SQ limit for single gap solar cells and the limiting efficiency of IBSCs are indicated as reference. All efficiencies are calculated using the detailed balance and assuming that solar cell are at 300 K and receive photons from the sun, modeled as a black body at 6000 K, at the maximum concentration of 46050 suns (after [Martí'09]).

According to Fig. 3.11, Ti and Fe may be useful to implement optimum GaAs-IBSCs, with limiting efficiencies close to 58%. This theoretical result motivated the research on IBSCs based on GaAs:Ti, which was supported by the *ab initio* calculus reported in [Wahnon'02]. That calculus predicted the formation of an IB inside the GaAs bandgap through the incorporation of large amount of Ti. GaAs-IBSCs were fabricated and characterized, for the first time, during the European project "IB materials and solar cells for PV with high efficiency and reduced cost" (IBPOWER) [Martí'09].

3.3.1 Experimental results in IBSCs based on GaAs:Ti

Highly efficient GaAs solar cells have been grown at around 600 °C using MBE reactors [Tobin'90]. For this reason, it seemed reasonable to use this growth technique to fabricate novel IBSCs based on GaAs:Ti. The manufacturing process of this material inside a MBE reactor requires the use of a Ti effusion cell operating at high temperature evaporation (up to 1700-1800 °C). This element was incorporated into a MBE reactor of the research group at the company RIBER (France) with the aim of fabricating the first

GaAs:Ti materials. The fabrication process faced the challenge of incorporating a very high Ti concentration inside the GaAs lattice. This process is intricate because the solubility of Ti in GaAs at $\sim 600^\circ\text{C}$ is lower than the required Ti concentration to form an IB ($6 \cdot 10^{19} \text{ cm}^{-3}$ [Luque'06a]) [Zhang'10]. However, since an inverse relationship exists between solubility and temperature, the incorporation of Ti above the Luque limit was possible using low growth temperatures, around $200\text{--}250^\circ\text{C}$ [Campion'03]. The GaAs layers grown at low temperature contains an excessive number of As anti-sites (As atoms that replace Ga atoms in the lattice crystal) [Zhao'05], which are undesired crystalline defects that act as lifetime killers. The concentration of these defects can be reduced by reducing the amount of As inside the MBE chamber. For this reason, the typical excess of As that is used during MBE growths [Tobin'90] was substituted by atomic Ga:As ratios close to 1:1 during the growth of GaAs at low temperature. The resulting growth rates were of $\sim 0.3 \mu\text{m/h}$.

Fig. 3.12: SIMS analysis performed on a GaAs:Ti sample grown by RIBER. The green and red curves represent the Ti concentration. A uniform Ti concentration slightly above $10^{20} \text{ at} \cdot \text{cm}^{-3}$ is measured throughout the first 300nm of the sample, which correspond to the thickness of the GaAs:Ti layer (after [García-Linares'13b]).

SIMS measurements corroborated that, in the GaAs:Ti layers, Ti was incorporated uniformly (Fig. 3.12). Furthermore, SIMS measurements also confirmed that in these layers the Ti concentration was proportional to the Ti partial pressure inside the reactor chamber, verifying the accurately controlled growth of these IB materials. GaAs:Ti layers were used to fabricate IBSC prototypes with the structure depicted in Fig. 3.13. In this structure, the GaAs:Ti layer ($1 \mu\text{m}$) was sandwiched between p-type GaAs emitter (450 nm) and n-type GaAs emitter (350 nm). These emitters were also grown inside the MBE of

RIBER, using standard growth conditions, with temperatures around 580 °C and an excess of As. The result was solar cells with a very simple structure, with neither window layers nor anti-reflecting coating. These elements were avoided because the main purpose of these devices was to verify the IBSC operating principles, reducing as much as possible the sources of spurious effects that could complicate the interpretation of the results and the manufacturing process.

Fig. 3.13: Artistic sketch of the layer structure of the IBSC prototypes based on GaAs:Ti fabricated by RIBER (after [García-Linares'13b]).

Two kinds of solar cells were fabricated by RIBER: IBSC prototypes with a structure as depicted in Fig. 3.13 and reference solar cells in which the IB material region was replaced by an un-doped GaAs layer grown at low temperature and without Ti. These devices were metalized with a grid designed for a concentration of 1,000 suns and they were characterized at IES-UPM. The main experimental results obtained with these solar cells are shown below.

The EQE of two representative solar cells, one IBSC prototype (red curve) and one reference solar cell (black curve) are shown in Fig. 3.14. These measurements indicate that both solar cells produce similar sub-bandgap photocurrents when they are illuminated with photons with energy lower than the GaAs bandgap (~ 1.42 eV). This sub-bandgap response cannot be attributed to optical transitions through DLs introduced by Ti atoms because it is slightly higher in the reference solar cell, in which Ti is not introduced voluntarily. However, the presence of sub-bandgap response is only possible if there are energy states inside the GaAs bandgap.

Fig. 3.14: EQE measurement at room temperature of a reference solar cell (black line) and an IBSC prototype (red line). Both cells show a sub-bandgap response from ~ 0.7 eV to 1.42 eV.

Energy states may emerge inside the GaAs bandgap as consequence of crystalline defects, such as As anti-sites. The presence of these defects is usual in GaAs grown at low temperature [Look'93], which can justify why a sub-bandgap response is obtained with the reference solar cell. In addition, the presence of crystalline defects can also justify why the supra-bandgap EQE of the two solar cells is so low ($< 10\%$) and why low bulk lifetimes, in the order of 3 ps, are necessary to fit the experimental results with PC1D [García-Linares Fontes'12]. Since the EQE of the IBSC prototype is lower than the EQE of the reference solar cell, especially at high photon energies, it is possible to affirm that recombination processes are stronger in the IBSC prototype. This may be due to a migration of Ti atoms into the emitter layers during the subsequent growth processes at high temperature (580 °C), where Ti atoms may act as lifetime-killers, or it may be due the incorporation of additional defects during growth because of the high reactivity of Ti.

The presence of states inside the bandgap can enhance the performance of a solar cell if these states lead to a power gain by means of sub-bandgap generation processes greater than the power loss by means of sub-bandgap recombination processes. This is the operating principle of an IB, where the nature of these electronic transitions is predominantly radiative. A priori, any energy state can have this capability, so we should not discard the possibility of the energy levels present inside the bandgap of the reference solar cell operate as an IB.

The sub-bandgap response obtained in Fig. 3.14 indicates that the energy levels located inside the GaAs bandgap are optically active. However, this is not enough to

conclude that these levels behave as an IB. On one hand, it is not clear whether these levels are isolated from the VB and the CB or they form a continuous density of states between them (this is depicted in Fig. 3.16 where it is assumed that energy levels emerge inside the GaAs grown at low temperature). On the other hand, it is not clear whether the sub-bandgap photocurrent is the result of pumping electrons from the VB to the CB via two-photon processes, or whether thermal generation and non-radiative mechanisms are involved. To test whether the sub-bandgap response is a consequence of thermal generation processes, low temperatures can be used during the characterization of the devices. Fig. 3.15 shows the photocurrent obtained by the reference solar cell when it is placed inside a He-cryostat to reduce its temperature down to 6 K. Similar results to those depicted in Fig. 3.15 are also obtained with IBSC prototypes.

Fig. 3.15: Photocurrent measurement, at 6 K, of a reference solar cell. Sub-bandgap response appears at lower energies than 1.5 eV, which is the GaAs bandgap at 6 K. (Courtesy of Dr. Elisa Antolín)

The photocurrent plotted in Fig. 3.15 is obtained by illuminating the solar cell with only monochromatic light whose energy is indicated on the x -axes. This figure indicates that, also at 6 K, photocurrent is produced by photon energies higher than 0.7 eV. The photocurrent produced at energies lower than 0.7 eV is not plotted in Fig. 3.15 because below this energy we cannot guarantee the validity of the measurement. For this reason we cannot determine if the absorption threshold is close to 0.7 eV or lower. An absorption threshold close to 0.7 eV may indicate the presence of energy levels close to the mid-gap of the GaAs, in which case the sub-bandgap response may be produced by two optical transitions, from the VB to the energy levels and from the energy levels to the CB. On the other hand, an absorption threshold below 0.7 eV may be the result of a continuous

density of states between the VB and the CB. If this were the case and the distance between the energy levels were lower than the thermal energy of the lattice at 6 K ($k_B T$), not only radiative processes could excite electrons, but also thermal processes related to electron-phonon interactions. These two possible distributions of the energy levels inside the GaAs bandgap are illustrated in Fig. 3.16. Both can explain the photocurrent measurements of Fig. 3.15 and the strong recombination that result in low bulk lifetimes of 3 ps (obtained from fitting the experimental results [García-Linares Fontes'12]).

Fig. 3.16: Sketch of two possible band diagrams for the reference solar cells studied in this Section. The terms HT and LT refer to the temperature at which the GaAs is grown, high and low respectively. On the left, energy levels close to the mid-gap provide an absorption threshold of around 0.7 eV, which is illustrated by the green arrows. On the right, a continuous density of states between the VB and the CB provide an absorption threshold below 0.7 eV, which is illustrated by the red arrows.

The analysis of the $J - V$ characteristics of solar cells can help us to determine the distribution of energy levels inside the GaAs bandgap and, therefore, what is the nature of the processes that produce the sub-bandgap response shown in Fig. 3.14 and Fig. 3.15. To this end, the $J - V$ characteristics of solar cells were measured under high irradiance levels and low temperatures. Both, reference solar cells and IBSC prototypes, showed similar $J - V$ characteristics to those plotted in Fig. 3.17.

Fig. 3.17: Normalized J-V characteristics of a IBSC prototype for different temperatures and illumination intensities (after [García-Linares'13b]).

Fig. 3.17 shows the $J - V$ characteristic of an IBSC prototype measured under different illumination conditions and at different temperatures. The black curve is obtained at room temperature by illuminating the samples with light from a xenon lamp that passes through AM1.5 filters. The red curve is obtained at the same temperature by illuminating the sample with high irradiance levels that come from a xenon flash, and the blue curve is obtained under the same high irradiances but at 20 K. Since these curves are strongly affected by the presence of non-ideal elements, such as high series resistance and low parallel resistance, J_L and the corresponding concentration factor X cannot be determined. This is the reason why Fig. 3.17 plots the normalized current density instead of J/X . This representation evidences the extreme increase of the V_{OC} of the IBSC prototype. At room temperature the V_{OC} recovers from 0.14 V to 0.69 V by the use of high irradiances, and at 20 K, the V_{OC} recovers up to 1.36 V. A similar tendency is observed in the V_{OC} of the reference solar cells which, in general, is higher than the V_{OC} of IBSC prototypes. The theory predicts that, under sunlight illumination, the V_{OC} of IBSCs must be lower than the V_{OC} of reference solar cells because an IB opens additional paths for recombination processes [Martí'08]. The theory also predicts that the eV_{OC} of IBSCs can exceed the absorption threshold and approach the value of the bandgap E_G [García-Linares'12; Martí'12]. This prediction is fulfilled by the IBSC prototypes and the reference solar cells studied in this Section, since the maximum eV_{OC} obtained with these solar cells, close to 1.4 eV, is higher than the absorption threshold (≤ 0.7 eV for temperatures in the 298-6 K range) [García-Linares'13b].

Given that the V_{OC} obtained with these solar cells approximates E_G/e , we can conclude that the energy levels located inside the GaAs bandgap do not form a continuous

density of states between the VB and the CB, since otherwise quasi-Fermi levels could not split up so much. Therefore, the experimental results suggest that, during the growth of GaAs at low temperature, energy levels emerge close to the mid-gap of the GaAs. This feature is also supported by the DLTS measurements shown in Section 5.4.1. According to this fact, the sub-bandgap response of Fig. 3.15 may be produced by two optical transitions, from the VB to the energy levels and from the energy levels to the CB.

It should be pointed out that the production of sub-bandgap photocurrent and the voltage preservation principle demonstrated in this Section are obtained under different illumination conditions. While the sub-bandgap photocurrent has been measured under low irradiance illumination, the voltage preservation has been demonstrated using high irradiances. This opens the door to the possibility that the energy levels inside the GaAs bandgap of the reference solar cell are optically active under low irradiance conditions, producing the sub-bandgap response of Fig. 3.15, and become optically inactive under high irradiance levels, providing the voltage recovery of Fig. 3.17. Besides, the low EQE of Fig. 3.14 and the poor performance provided by the solar cells indicate that the additional generation processes introduced by the energy levels do not compensate the additional recombination processes. The maximum efficiency obtained with these solar cells is 2.9%, which is significantly lower than the 6.5% efficiency simulated with PC1D for a solar cell with the same structure but without energy levels inside the GaAs bandgap [García-Linares Fontes'12].

3.4 Summary

In this Chapter we have researched IBSCs based on DLs. In particular IBSCs based on Si:Ti and GaAs:Ti materials.

The first IBSC prototypes based on Si:Ti have been fabricated combining ion implantation and PLM techniques, thanks to a collaboration between the UCM and the UPC. These devices have been characterized at IES-UPM where EQE measurements have revealed the presence of a sub-bandgap response associated to DLs introduced during the Ti implantation process. This sub-bandgap response, generated when the IBSC prototypes are illuminated with photon energies from 0.75 eV to 1 eV, is probably the result of optical transitions between the VB and the IB and tunneling-emission from the IB to the CB. This is supported by the fact that sub-bandgap response is reduced when the lateral distance between the IB and the CB of the n-emitter is increased. This tunnel effect reduces the effective bandgap of the Si:Ti material to $E_H \approx 0.75\text{eV}$, which seems to be the reason why the maximum achievable V_{OC} of the IBSC prototypes, around 0.52 V, is significantly lower than the maximum V_{OC} obtained with reference solar cells, which is 0.83 V. As a consequence, the voltage preservation principle is not fulfilled by the IBSC prototypes

based on Si:Ti. In order to obtain prototypes that operate as real IBSCs, it is necessary to completely suppress the tunneling effect by increasing the thickness of the intrinsic a-Si:H layers. In addition, it is recommendable to increase the thickness of the Ti implanted layer to increase the sub-bandgap response and make it useful for PV applications. However, this must not be accompanied by an increase in Ti tails, where the Ti-concentration is below the Luque limit. Otherwise, the increase in carrier generation may not compensate the increase in carrier recombination.

The first IBSC prototypes based on GaAs:Ti have been manufactured by the MBE reactor of the research group at the company RIBER (France). SIMS measurements have revealed that Ti can be incorporated inside the GaAs lattice at a concentration above the Luque limit, using low growth temperatures of 200-250°C. Photocurrent measurements have evidenced sub-bandgap response, providing absorption thresholds ≤ 0.7 eV at temperatures as low as 6 K. Similar results have been obtained in reference solar cells. This indicates that the sub-bandgap response is a consequence of crystalline defects that emerge inside the GaAs grown at low temperature, introducing DLs inside the GaAs bandgap. These DLs have not limited the output voltage of the solar cells, since eV_{OC} above the absorption threshold has been obtained (up to 1.36 eV). The analysis of the experimental results has indicated that the DLs responsible of the sub-bandgap response are located close to the mid-gap of the GaAs and participate in two-photon generation processes. However, the low EQE and the poor performance of these solar cells indicate that the additional recombination processes introduced by the DLs are stronger than the additional generation processes.

In addition to these experimental results, results obtained with the detailed balance have revealed that, under concentrated sunlight, Si-IBSCs can be more efficient than conventional Si solar cells. Besides, contrary to what is conventionally assumed, these results have demonstrated that non selective absorption coefficients can lead to higher efficiencies than those obtained with selective absorption coefficients. This happens if the IB is placed at positions deeper than the optimum one. The reason is because, for that IB-positioning, non-selective absorption coefficients can lead to a better match between the sub-bandgap transitions $VB \rightarrow IB$ and $IB \rightarrow CB$.

4 RESEARCH IN IBSC BASED ON QUANTUM DOTS

4.1 Introduction

When IB materials are based on quantum dots (QDs), the position of the IB is defined by the position of the less energetic confined state in the CB, named ground state (GS) (Fig. 1.8). The set of GSs corresponding to several QDs have the capacity of operating as an IB. However, this IB does not need to be a real band since the wave functions of confined states do not need to extend to the all material lattice [Martí'13]. From the point of view of the IBSC concept, the use of QDs can be advantageous thanks to the phenomenon known as the “phonon-bottleneck effect”. The basis of this phenomenon is that non-radiative recombination through confined states is unlikely to occur via electron-phonon interactions. This feature helps optical transitions dominate the generation and recombination processes in QD-IBSCs [Cuadra'04a]. Some authors support this phenomenon on the grounds that non radiative recombination through confined states requires several phonons to be involved in the process, which is rather ineffectual in QDs [Jiang'98]. Nevertheless, the “phonon-bottleneck effect” has as many defenders as detractors, as pointed out by Nozik in [Martí'03].

In QD-IBSCs, the sub-bandgap transitions provide useful work when optical generation processes dominate. The photons responsible for the generation processes need to come from a source hotter than the cell, otherwise, generation processes that may take place will do so but without resulting in electrical work [Luque'01;Luque'02]. This is the case of generation processes by means of thermal-photons, coming from the lattice or the surroundings at thermal equilibrium. This generation process is known as “thermal

escape” and it does not contribute to generate useful work [Fry’00]. Thermal escape is detrimental for QD-IBSCs because, in spite of it not impeding the optical generation by photons coming from “hot” sources, it increases the carrier recombination. This is explained in [Martí’06b], in terms of the value of the saturation current density J_0 since the value of this parameter is a consequence of the thermal generation. In that work the authors conclude that a saturation current density J_0 as high as $9 \text{ mA} \cdot \text{cm}^2$ is obtained for a cell with a bandgap of 0.2 eV, operating at 300 K in the radiative limit. In QD-IBSCs, the IB-CB transitions can be characterized by high J_0 at room temperature, close to $9 \text{ mA} \cdot \text{cm}^2$ [Martí’06b]. This seems to explain why, at this temperature, photocurrent generated via two-photon processes has not been detected, because in spite of VB-IB and IB-CB transitions taking place, the generated carriers can be strongly recombined from the IB to the CB.

In type-I QDs, the proximity between GS and excited states (ES) increases the thermal escape of electrons from GS to the extended states of the host semiconductor. The thermal escape must be minimized for the reason mentioned above. One possible way of achieving this consists of reducing the temperature of the QD-IBSC prototypes and its surroundings, which has been used to demonstrate some of the operation principles of IBSCs [Antolin’10]. Another possibility consists of increasing the energetic distance between GS and ES, which has been obtained in QD systems based on wide-bandgap host semiconductors, such as InAs/AlGaAs QDs [Ramiro’12]. Besides, the use of materials with higher bandgaps allows the shifting towards bandgap distributions close to the optimum ($E_G = 1.95 \text{ eV}$, $E_L = 0.71 \text{ eV}$ and $E_H = 1.24 \text{ eV}$).

In this Chapter we will present our contribution to the research on InAs/AlGaAs QD-IBSC prototypes, in collaboration with the University of Tokyo. In particular, we will show the advances obtained in the demonstration of the IBSC operating principles at room temperature.

4.2 Spectral resolution of sub-bandgap transitions

The research in QD-IBSC prototypes did not take long to demonstrate the production of sub-bandgap photocurrent. The sub-bandgap response at room temperature, reported in several works [Luque’04;Okada’11], has usually been detected for photon energies higher than E_H . This photocurrent has usually been associated to a combination between optical transitions from the VB to the IB and thermal escape or tunneling emission from the IB to the CB [Antolin’10;Ramiro’15]. Due to the presence of these undesired mechanisms (thermal escape and tunneling emission), the direct characterization of E_L has been missing in QD-IBSC prototypes until 2014, when it was reported, for the first time, in [Ramiro’14a]. In that work E_L was spectrally resolved by

illuminating QD-IBSCs simultaneously with low energy photons, capable only of pumping electrons from the IB to the CB, and photons with energy capable of pumping electrons from the VB to the IB. In this section we will provide the spectral resolution of E_L obtained, for the first time, by illuminating a QD-IBSC prototype solely with low energy photons, only capable of pumping electrons from the IB to the CB [Datas'15]. A priori this fact is contrary to the operation of an ideal IBSC. However, as we will see next, it agrees with the operation of a real IBSC.

The results reported in this section correspond to QD-IBSC prototypes based on InGaAs/Al_{0.2}Ga_{0.8}As QDs and grown by MBE at the University of Tokyo. The device structure has been processed at IES-UPM, where the front and back contacts were deposited using conventional photolithographic techniques and thermal evaporations. The devices studied in this section (Fig. 4.1 a) contain a n-type "field damping layer" (FDL) next to the front p-emitter whose doping and thickness are designed to sustain most of the depletion region. As a consequence, the QDs are located within a flat band potential region, as is illustrated in Fig. 4.1 (b) [Martí'08]. This situation is considered advantageous for solar cell operation because it prevents the tunneling emission of electrons from the IB to the CB [Antolin'10] and makes it possible to partially fill the IB with electrons coming from the silicon doping of the QD super-lattice [Martí'08]. The incorporation of one donor impurity per QD guarantees both, empty states in the IB to receive electrons from the VB and filled states in the IB to supply electrons to the CB [Martí'08].

Fig. 4.1: (a) Layer structure of the QD-IBSC prototypes based on InAs/ $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ QDs and (b) their idealized band diagram in short-circuit conditions considering finite carrier mobility. (after [Datas'15])

Fig. 4.2 shows the short-circuit photocurrent density produced by a QD-IBSC prototype under illumination by monochromatic light. This monochromatic light is the result of diffracting the light of a lamp inside a 1/4 monochromator. The photocurrents of Fig. 4.2 are modulated by the lamp spectrum used in the setup⁹ and correspond to two different cell temperatures, 300 and 20 K. At 300 K, the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ bandgap is identified at 1.7 eV because of the abrupt change in the photocurrent density at that energy, which is in agreement with the theoretical $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ bandgap [Levinshtein'99]. At this temperature a sub-bandgap photocurrent density is detected when the solar cell is

⁹Two lamps are used to obtain the measurements of Fig. 4.2: an infrared lamp (silicon carbide lamp) for photon energies between 0.2 eV and 0.9 eV and a halogen lamp for photon energies between 0.9 eV and 3 eV (100 W QTH lamp).

illuminated with photon energies below 1.71 eV. Previous works [Antolin'10;Jolley'12] have justified this sub-bandgap photocurrent as the result of two pumping-processes: optical transitions of electrons from the VB to the IB and a thermal escape process from the IB to the CB. We can use the same argument to explain the sub-bandgap photocurrent density obtained at 300 K (red line in Fig. 4.2) since this photocurrent density is significantly reduced when the temperature of the solar cells decreases to 20K (blue line in Fig. 4.2), once the thermal excitation is reduced. According to this argument, it is possible to identify E_H as the photon energy at which the sub-bandgap photocurrent abruptly decreases (~ 1.17 eV).

Fig. 4.2: Spectral photocurrent density obtained when the QD-IBSC prototype is only illuminated with the monochromatic light that comes from the output of a monochromator, at 300K and 20K. (after [Datas'15])

The spectrally resolution of E_L requires that not only IB→CB transitions take place, but also VB→IB transitions. A priori, under monochromatic illumination and low temperature, it is difficult to resolve E_L because it is unlikely that generation processes between the VB and the IB take place for photon energies below E_H . However, in Fig. 4.2 a sub-bandgap photocurrent density is obtained at 20 K for photon energies between 0.25 eV and 0.55 eV (below E_H), which should be related to the IB-CB transition and consequently with E_L . According to our knowledge, this is the first time that a QD-IBSC prototype produces photocurrent when illuminated solely by a monochromatic light which is only capable of pumping electrons from the IB to the CB [Datas'15].

To understand how the illumination with photon energies below E_H can generate a measurable photocurrent in a QD-IBSC prototype, it is necessary to analyze the equivalent circuit (explained in section 1.1.1) that illustrates the operation of a real IBSC in short-circuit conditions (Fig. 4.3a). In a real IBSC, in which carriers have finite mobilities, the quasi-Fermi levels split up within the device even in short-circuit conditions, as illustrated in Fig. 4.1 (b). This is taken into account in the circuit of Fig. 4.3 (a) by the resistance R_s , that makes it possible for diodes D1, D2 and D3 to become biased when the device is illuminated under short-circuit conditions. As a result, through each diode, a current density flows according to the Shockley's equation [Shockley'61]:

$$J_{Di} = J_{0i} \left(\exp\left(\frac{eV_i}{mk_B T}\right) - 1 \right) \quad (4.1)$$

where V_i is the bias voltage associated to each diode, J_{Di} is the current density through each diode, J_{0i} is the diode saturation current density and m is the ideality factor, which will be considered as 1 hereinafter.

Since IB-CB transitions produce low photocurrent density ($\sim 10^{-10} \text{ A} \cdot \text{cm}^{-2}$), the circuit of Fig. 4.3 (a) can be simplified to the small-signal equivalent circuit in Fig. 4.3 (b) to describe the operation of the QD-IBSC prototype. This circuit is constructed by replacing diodes D_i by their equivalent small signal resistances r_i .

Fig. 4.3: (a) Simplified IBSC equivalent circuit in short-circuit conditions. (b) Small signal circuit that describes the operation under an illumination that only can cause IB to CB transitions (after [Datas'15]).

According to the circuit of Fig. 4.3 (b), the sub-bandgap photocurrent density obtained when the QD-IBSC prototype is illuminated with photons with energy in the 0.25-0.55 eV range is detected thanks to a current density j_{D2} that flows from the VB to the IB. The operation described by the circuits of Fig. 4.3 is in agreement with the experimental results shown in Fig. 4.4. These results are obtained by illuminating the solar cell with two different sources, a monochromatic light whose photon energy is higher than E_G and a

broadband infrared (IR) source whose photon energies are lower than E_H (produced by a blackbody IR emitter filtered with a GaSb wafer). As is illustrated in Fig. 4.4 (a), the monochromatic light continuously illuminates the solar cell, producing a short-circuit photocurrent density (J_{ph} in Fig. 4.3a) that determines the bias point of each diode, D1, D2 and D3. The intensity of this monochromatic light varies, changing the bias points. As a consequence, the small current density generated by the chopped IR light ($j_{ph}^{(3)}$) also varies, in spite of the intensity of this light remaining constant (j_{L3} is constant). This variation is plotted in Fig. 4.4 (b), where the experimental data (grey triangles) are represented together with the results simulated with the circuital model.

Fig. 4.4: (a) Experimental setup used to obtain the IR photocurrent density generated in the QD-IBSC prototype as a function of supra-bandgap photocurrent density. The supra-bandgap photocurrent density, J_{ph} , is obtained, momentarily, by placing the chopper at the monochromator output. (b) The experimental results (grey triangles) and the simulated results (grey line) are plotted together with the current density that flows

through each diode (D1, D2 and D3) (after [Datas'15]).

Fig. 4.4 (b) shows the short-circuit current density produced by an infrared source (solid grey line) and the current densities flowing through D1 (blue line), D2 (green line) and D3 (red line). These current densities are obtained with the circuit model of Fig. 4.3, assuming that $R_s = 51.8 \text{ k}\Omega \cdot \text{cm}^2$, $j_{L3} = 2.44 \cdot 10^{-8} \text{ A/cm}^2$, $J_{01} = 2.64 \cdot 10^{-80} \text{ A/cm}^2$, $J_{02} = 4.65 \cdot 10^8 \cdot J_{01}$ and $J_{03} = 20.19 \cdot J_{02}$. As J_{ph} increases, the drop in voltage in R_s increases, which bias D1, D2 and D3 at different voltages. Three different regimens can be observed in Fig. 4.4 (b): (1) For $J_{ph} < 10^{-9} \text{ A/cm}^2$, D2 operates near short-circuit and D3 is in the direct-bias regime, so that D3 recombines the major part of the infrared photocurrent j_{L3} . As a result the measured $j_{ph}^{(3)}$ is low. (2) For $10^{-9} < J_{ph} < 5 \cdot 10^{-7} \text{ A/cm}^2$, D2 enters in the direct-bias regime and reduces its equivalent resistance (r_2). As a result, j_{D2} and $j_{ph}^{(3)}$ increase. (3) For $J_{ph} > 5 \cdot 10^{-7} \text{ A/cm}^2$, D1 enters in the direct-bias regime, recombining most of j_{L3} and reducing the measured $j_{ph}^{(3)}$. The simulated $j_{ph}^{(3)}$ (grey line) describes the same tendency as the experimental data (grey triangles), except for the abrupt decrease at high J_{ph} . While the simulated $j_{ph}^{(3)}$ drops sharply to zero due to the ideal characteristic of D1, the experimental $j_{ph}^{(3)}$ follows a softened decay. This fact may happen due to the existence of several recombination mechanisms (radiative, Auger, Shockley-Read-Hall, etc.), which have been omitted to reduce the number of elements in the equivalent circuit. The possible variation of the QD absorption, resulting from variations in the electron occupancy of the IB under different illumination conditions, has been also omitted to simplify the qualitative explanation of the experimental results.

The results shown in Fig. 4.4 seem to validate the hypothesis that at 20 K the photocurrent generated by IB-CB transitions is detectable thanks to the saturation current between the VB and the IB (J_{02}) being high enough to be measured. The parameters used to describe the experimental results imply that $J_{03} > J_{02}$ so that, a priori, it should be easier to detect the photocurrent generated by VB-IB transitions. However, at 20 K the photocurrent measured between E_H and E_G is lower than the photocurrent measured at 0.35 eV. This can only be explained assuming that the photocurrent generated by transitions VB-IB (j_{L2}) is lower than the photocurrent generated by transitions IB-CB (j_{L3}). A possible explanation is that at 20 K the absorption coefficient α_{VI} is lower than the absorption coefficient α_{IC} . This may be possible in devices such as ours, where the IB is located within a flat band potential region (Fig. 4.1b). Since in these conditions, lower temperatures may lead to higher electron occupancy in the IB, facilitating IB-CB transitions at the expense of VB-IB transitions. However, we are not sure whether the intensity of the monochromatic light at photon energies between E_H and E_G is higher than the intensity at 0.35 eV, so we cannot infer conclusions about the absorption coefficients.

4.3 IBSC operating principles at room temperature

To date, the use of low temperature has been required to demonstrate some of the IBSC principles in prototypes based on QDs, because of the thermal escape between the IB and the CB [Antolín'08;García-Linares'13a]. However, demonstrating these principles at room temperature (RT) may also be possible if the intensity of thermal escape is reduced by using barrier materials with higher bandgaps [Ramiro'12]. In this respect we have manufactured, in collaboration with the University of Tokyo, InAs QDs based on AlGaAs barriers with a concentration of aluminum slightly higher than the one used in previous works (Al content of 30% instead of 20%-25%) [Datas'15;Ramiro'14a].

The layer structure of the solar cells studied in this section has been grown by MBE at the University of Tokyo. The device has been processed at the IES-UPM, where the metal contacts have been deposited by thermal evaporation. The result is the device structure sketched in Fig. 4.5 (a). Two different types of samples have been characterized, samples with 25 layers of InAs/ $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ QDs and reference samples with $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ occupying the volume that in the previous sample is occupied by the QD layers. These solar cells have neither a FDL nor an intentional doping in the region where the QDs are located. As a consequence, in the QD-IBSC prototypes the QDs are located inside the space-charge region. Under these circumstances the electron occupation of the IB states is ruled by their location inside this region, as illustrated in Fig. 4.5 (b). This situation warranted that, in equilibrium, some QD layers are partially filled with electrons on prize that others are either filled or emptied of electrons [Marti'08]. In order to demonstrate the IBSC operating principles at RT, the solar cells have been characterized by means of photocurrent measurements and current-voltage curves under concentrated white-light illumination. The experimental results are shown below.

Fig. 4.5: (a) Layer structure of the QD-IBSC prototypes based on InAs/ $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ QDs. (b) The localization of

QDs inside the space-charge region rules the effective population of the IB (after [Martí'08]).

Fig. 4.6 shows the short-circuit photocurrent density produced by two representative solar cells, a QD-IBSC prototype and a reference solar cell. These measurements are performed by illuminating the samples with the monochromatic light that results from diffracting the light of a halogen lamp (100 W QTH lamp) inside a 1/4 monochromator. Since the photon energies used to illuminate the samples are in the 0.2-1.4 eV range, below the $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ bandgap (1.8 eV [Levinshtein'99]), the photocurrent must be related to energy levels within the bandgap, which are intentionally introduced only in the solar cell with QDs. The spectral photocurrent of the two samples is measured at RT under two different operation conditions: with and without illumination by means of a continuous-wave (cw) laser diode of 1.32 eV (energy lower than E_G). The results obtained are shown in Fig. 4.6, where the photocurrents obtained at 20 K without using the light bias are also plotted.

Fig. 4.6: Spectral photocurrent density obtained with a QD-IBSC prototype (red curves) and a reference solar cell (dark curves) at RT and 20 K (black curves). The photocurrent at RT is measured under two different operation conditions: with (solid lines) and without (dashed lines) illumination by means of a cw laser diode of 1.32 eV whose energy lower than E_G . (after [López'16]).

An unexpected below bandgap photocurrent appears in Fig. 4.6 when the reference sample is illuminated with photon energies from 1.2 to 1.4 eV (dashed black line). This photocurrent, which does not change under the illumination with the 1.32 eV bias light (solid black line), must be related to the presence of native defects in the $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$, such as DX centers. These defects are usually present in samples with Al fractions above 30% [Pavesi'94].

The measurements of Fig. 4.6 reveal a notable sub-bandgap photocurrent generated in the QD-IBSC prototype. The photocurrent generated when the QD solar cell is illuminated only with monochromatic photon energies from 0.9 to 1.4 eV (dashed red line in Fig. 4.6) disappears when the temperature decreases down to 20 K (solid blue line in Fig. 4.6). This seems to indicate that this sub-bandgap photocurrent is the result of two pumping-processes: optical transitions of electrons from the VB to the IB and a thermal escape from the IB to the CB. The suppression of sub-bandgap photocurrent at 20 K suggests that the absorption coefficients associated to sub-bandgap generation processes do not overlap at low temperature. These absorption coefficients depend on the electron concentration in the IB, which in the case of our QD-IBSC prototype is determined by the location of the IB inside the space-charge region. Therefore, absorption coefficients associated to sub-bandgap transitions should not change significantly with temperature, and consequently they should not overlap at room temperature either. According to the results at RT, we can identify E_H as the photon energy at which the sub-bandgap photocurrent (dashed red line in Fig. 4.6) decreases abruptly (~ 1.17 eV). However, to resolve E_L we need to pump electrons from the VB to the IB by illuminating the sample with additional photons with energy above E_H . This is how the results represented by the solid red line in the Fig. 4.6 have been obtained. In this case, a cw laser diode of 1.32 eV has been used to continuously illuminate the solar cell, producing a continuous photocurrent density of $0.52 \text{ mA} \cdot \text{cm}^{-2}$, equivalent to 0.5 suns illumination. Under these illumination conditions, the QD-IBSC prototype shows an absorption threshold of 0.3 eV and an increase in photocurrent for photon energies below 1.17 eV. This increase in photocurrent is a consequence of a two-photon generation process, which is one of the operating principles of the IBSC.

The results of Fig. 4.6 can be described by the equivalent circuit of Fig. 4.7, which illustrates the operation of the QD-IBSC prototype in short-circuit conditions at RT. Notice that, contrary to the equivalent circuit used in section 4.2 (Fig. 4.3), in the equivalent circuit of Fig. 4.7 the series resistance has been omitted. The reason is that, in this case, the IB is located inside the space-charge region where the split of quasi-Fermi levels can be considered zero under short-circuit conditions. In Fig. 4.7 the presence of thermal escape at RT is represented by a small equivalent resistance r_{th} in the small-signal model of the circuit. This small r_{th} facilitates the production of photocurrent ($J_{ph} = 0.52 \text{ mA/cm}^2$) when a light bias with energy $E_H < E < E_G$ illuminates the QD-IBSC prototype (Fig. 4.7b). As result of this illumination, the diode D2 becomes biased in forward and reduces the value of its equivalent small-signal resistance, r_2 . This reduction leads to an increase in the current density that flows through r_2 (j_{D2}), which corresponds to the measured photocurrent density (j_{ph}) when the QD-IBSC prototype is illuminated with photons that pump electrons from the IB to the CB (Fig. 4.7c). When the device is illuminated with photons that pump electrons from the VB to the IB, the measured photocurrent

corresponds to the current flowing through r_{th} , which value does not change significantly when r_2 is reduced (Fig. 4.7d).

Fig. 4.7: (a) Sketch of the experimental setup used to measure the photocurrent produced with and without light bias. (b) Simplified IBSC equivalent circuit in short-circuit conditions. (c) Small-signal circuit that describes the operation under an illumination that only can cause IB to CB transitions. (d) Small-signal circuit that describes the operation under an illumination that only can cause VB to IB transitions. Thermal escape is taken into account by means of a small r_{th} .

The discussion above explains why at RT the sub-bandgap photocurrent produced by the QD-IBSC prototype increases in the 0.3-1.17eV range under the illumination of the light bias, as a consequence of two-photon absorption. According to this, the absorption threshold of the solid red line of Fig. 4.6 may represent an upper bound for E_L . Therefore, we can estimate the two sub-bandgaps as $E_L \approx 0.3 \text{ eV}$ and $E_H = 1.17 \text{ eV}$. Taking into account that E_G is around 1.8 eV [Levinshtein'99], a VB QD offset of around 0.33 eV can be

inferred. These results, in which both sub-bandgap transitions are spectrally resolved for the first time at RT, are reported in [López'16]. They have been obtained thanks to: (1) Increasing the intensity of the monochromatic light that illuminates the samples, which is approximately two orders of magnitude greater than the one used in the section 4.2. (2) Increasing the Al concentration with respect to previous devices [Datas'15;Ramiro'14a], which reduces the thermal escape by enlarging the bandgap E_G . Notice that, in spite of using larger values for E_G , thermal escape is not suppressed in the QD-IBSC prototypes studied in this section. However, in this case, the presence of thermal escape does not prevent the detection of photocurrent at RT by means of IB-CB optical transitions. These transitions are detected in a wide energy range, from E_L to E_H (Fig. 4.6), contrary to what happens with the solar cells studied in the previous section, in which IB-CB transitions are detected in a narrow energy range, from 0.2 to 0.55 eV (Fig. 4.2). This difference can be due to the use of different lamps to illuminate the samples. While in the previous section the photocurrent corresponds to the spectrum of light from an IR lamp (silicon carbide lamp), in this section the photocurrent corresponds to the spectrum of light from a halogen lamp (100 W QTH lamp).

Fig. 4.8 shows the $J_{SC} - V_{OC}$ curves obtained with the QD-IBSC prototype and the reference solar cell under different irradiance levels. These curves are measured at RT using the experimental technique described in section 2.3.3 [Linares'12].

Fig. 4.8: J_{SC} vs. V_{OC} at RT for different levels of illumination. The maximum concentration achieved is ~ 390 suns. (after [López'16])

Fig. 4.8 shows that the V_{OC} produced by the QD-IBSC prototype at RT covers the range from 0.73 to 1.07 V when the sample is illuminated by a Xenon lamp with irradiance

levels from 0.5 to ~ 390 suns. These values do not differ significantly from those obtained in previous QD-IBSC prototypes [Ramiro'14a]. However, for the first time, the V_{OC} clearly surpasses the absorption threshold at RT without requiring the use of high irradiances [López'16]. This demonstration is possible thanks to the fact that the absorption threshold of our device is the lowest obtained at RT, since it corresponds to $E_L \approx 0.3$ eV.

An important observation is that both phenomena, the production of photocurrent by two-photon absorption and the production of an output voltage that exceeds the absorption threshold, have been demonstrated, for the first time, under similar conditions of temperature and illumination. The absorption threshold of 0.3 eV and the V_{OC} of 0.73 V have been measured at RT under illumination conditions which imply similar photocurrent generations. In both cases the light that illuminates the sample produces a photocurrent density of around $0.52 \text{ mA} \cdot \text{cm}^{-2}$, which is equivalent to the photocurrent density generated by 0.5 suns. However, in order for QD-IBSC prototype to provide a efficiency higher than that of the reference solar cell, it is necessary that the V_{OC} surpasses both sub-bandgaps, E_L and E_H . This has not been fulfilled because thermal escape has not been totally suppressed.

4.4 Summary

In this Chapter we have studied QD-IBSC prototypes grown by MBE at the University of Tokyo. Two semiconductor structures have been fabricated using AlGaAs as barrier material. Since this material has a tunable bandgap that increases as Al concentration increases, it can be used to fabricate QD-IBSCs in which thermal processes do not dominate the sub-bandgap transitions [Antolín'08;García-Linares'13a].

The first semiconductor structure studied contains InAs/ $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ QDs located within a flat band potential region, where the IB is partially filled with electrons coming from the silicon doping of the QD super-lattice. In this structure the presence of thermal processes has prevented the detection of IB-CB transitions at room temperature. These transitions have been detected at low temperature, which has led to the spectral resolution of E_L , for the first time, by illuminating the QD-IBSC prototypes solely with low energy photons, only capable of pumping electrons from the IB to the CB [Datas'15]. Experimental results suggest that, under these illumination conditions, the spectral resolution of E_L is possible thanks to the saturation current between the VB and the IB is high enough to be measured.

In order to work towards the demonstration of the IBSC operating principles at room temperature, the second semiconductor structure has been manufactured with an Al concentration slightly higher than that used previously (Al content of 30% instead of

20%). This structure contains InAs/Al_{0.3}Ga_{0.7}As QDs located within the space-charge region, so that the effective population of the IB is ruled by their location inside this region. These devices have been characterized by photocurrent measurements and current-voltage curves under concentrated white-light illumination. Experimental results have demonstrated the production of photocurrent by means of the absorption of two-photons, for the first time at room temperature [López'16], in spite of the presence of thermal escape. As a consequence, these devices have provided the lowest absorption threshold measured at room temperature in a QD-IBSC, which corresponds to $E_L \approx 0.3$ eV. This fact has facilitated the demonstration that the V_{OC} produced by the QD-IBSC prototypes can clearly surpass the absorption threshold at room temperature without requiring the use of high irradiances [López'16]. Both principles, the production of two-photon photocurrent and the production of an output voltage that exceeds the absorption threshold, have been demonstrated under similar illumination conditions equivalent to 0.5 suns. In spite of the mentioned advances, in these devices the thermal escape is so strong that at room temperature eV_{OC} cannot overcome both sub-bandgaps (E_L and E_H), which is necessary for the limiting efficiency of QD-IBSCs to surpass the SQ limit.

5 IMPLEMENTATION OF CAPACITIVE TECHNIQUES FOR THE INTERMEDIATE BAND CHARACTERIZATION

5.1 Introduction

Capacitive techniques such as photo-capacitance measurements [Henry'73] or deep level transient spectroscopy (DLTS) [Lang'74] have usually been used to study energy levels inside the bandgap of semiconductors. As illustrated in Fig. 5.1, these levels have the capability of participating in excitation processes from the VB (1), excitation processes from the energy level (2), de-excitation processes from the CB (3) and de-excitation process from the energy level (4). From the point of view of energy levels inside the bandgap, processes (1) and (4) are interpreted as emission and capture of holes respectively, and processes (2) and (3) are interpreted as emission and capture of electrons respectively. Depending on the rate of each of these processes, energy levels inside the bandgap can act predominantly as recombination centers (if in Fig. 5.1 $c_n n, c_p p \gg e_n, e_p$) or as carrier traps (if in Fig. 5.1 $c_n n, e_n \gg c_p p, e_p$ or $c_n n, e_n \ll c_p p, e_p$) [Schroder'06].

Fig. 5.1: Band diagram for a semiconductor with energy levels inside the bandgap. The capture and emission process are illustrated in the figure.

Carrier traps interact predominantly with only one energy band, the CB or the VB, by means of capture and emission processes of electrons and holes respectively. These processes modify the charge state of the trap centers, so that acceptor-traps and donor-traps become negatively charged and positively charged when they capture electrons and holes respectively. For this reason, the presence of carrier traps inside the depletion region of semiconductor devices, also called space-charge region (SCR), can modify the localized charge density of the SCR [Blood'92b]. This will be explained in detail in Section 5.2.1.

Semiconductor devices such as Schottky diodes or p-n junctions have a capacitance associated to the SCR (the depletion capacitance), which is a parameter that can be measured by capacitive techniques [Barnes'02]. When we apply these techniques to Schottky diodes or to abrupt asymmetric p⁺-n or n⁺-p junctions, we can consider that the SCR extends mainly to one semiconductor region, the less doped one in the case of asymmetric p-n junctions. According to the depletion approximation [Blood'92a], the depletion capacitance of devices in which the SCR extends to one semiconductor region is [Blood'92a]:

$$C = A \frac{dQ}{dV} = A \frac{\varepsilon \varepsilon_0}{x_{\text{SCR}}} = A \sqrt{\frac{\varepsilon \varepsilon_0 e}{2}} \cdot \sqrt{\frac{N_{\text{SCR}}}{V}} \quad (5.1)$$

where A is the area of the device, ε is the relative semiconductor permittivity, ε_0 is the vacuum permittivity, x_{SCR} is the width of the SCR, N_{SCR} is the charge density of the SCR divided by the electron charge and V is the total band bending along the device and, therefore, the sum of the built-in voltage (V_{bi}) and the applied bias (V_a): ($V = V_{\text{bi}} + V_a$)¹⁰.

¹⁰Note that a forward bias (V_f) has opposite sign to V_{bi} and reduces the overall band bending ($V = V_{\text{bi}} - V_f$), and a reverse bias (V_r) has the same sign that V_{bi} and increases the overall band bending ($V = V_{\text{bi}} + V_r$).

The capacitive techniques of this Chapter are based on measuring the depletion capacitance by means of small-signal voltages. These techniques are described in Section 5.2, where we will see how they use the dependence of C on N_{SCR} to obtain information of carrier traps present inside the SCR of the devices under study.

The application of capacitive techniques to IB materials requires, first of all, to extend the theory behind these techniques to IB-states instead of conventional carrier traps. This will be done in Sections 5.2. In addition, the implementation of experimental set-ups at IES-UPM is also required, in particular, a DLTS set-up. This will be detailed in Section 5.3. The experimental results obtained with these set-ups will be summarized in Section 5.4. These results will be useful to complement the study of the energy levels that form the IB of the IBSC prototypes analyzed in this Thesis. Specifically, these results will determine the strength of carrier capture processes that involve the IB, in terms of the capture cross sections of IB-states.

5.2 Description of the capacitive techniques

In this Section we will describe the capacitive techniques used to obtain the experimental results of the following Sections. These techniques are: Capacitance-voltage (CV) measurements and DLTS.

5.2.1 Capacitance-voltage (CV) measurements

Conventional CV measurements are usually carried out in Schottky diodes or abrupt asymmetric p^+-n or n^+-p junctions, where the small-signal depletion capacitance (C) can be approximated by equation (5.1) [Blood'92a]. According to this equation, the depletion capacitance depends on the width of the SCR (x_{SCR}), which in turn depends on the applied bias (V_a) and the charge density of SCR (eN_{SCR}). Therefore, if the area of the device under study is known (A), the value of the measured C can determine the thickness of the SCR (x_{SCR}). In addition, if C is measured at different V_r and these data are represented as C^{-2} versus V_r , the profile of $N_{\text{SCR}}(x)$ can be obtained from the local slope of the plot. This procedure is useful to obtain any distribution of the charge density [Hillibrand'60], whether homogeneous or inhomogeneous, since the charge fluctuation associated with the measured capacitance corresponds to $N_{\text{SCR}}(x \rightarrow x_{\text{SCR}})$ [Blood'92b].

N_{SCR} is the net charge density divided by the electron charge. Generally, this parameter is the result of adding the positive charge density of ionized donor dopant impurities (N_D^+), the positive charge density of donor-traps occupied by holes (p_T), the

negative charge density of ionized acceptor dopant impurities (N_A^-) and the negative charge density of acceptor traps occupied by electrons (n_T) [Blood'92b].

$$N_{SCR} = N_D^+ + p_T - N_A^- - n_T \quad (5.2)$$

In conventional n-type and p-type semiconductors, trap concentrations are usually lower than the doping concentration. For this reason, the value of the N_{SCR} obtained from CV measurements is usually associated to N_D^+ and N_A^- respectively. Since dopant impurities introduce shallow levels, which are completely ionized at room temperature ($N_D^+ \approx N_D$ and $N_A^- \approx N_A$), we usually identify the value of N_{SCR} as the density of dopant impurities [Hillibrand'60].

5.2.1.a CV measurements in IB materials

As was mentioned in Section 1.1.3, in ideal IB materials the number of IB-states per unit of volume (N_I) must be higher than possible variations of IB-electron concentration and IB-hole concentration, in order to maintain ε_{FIB} inside the IB [Marti'12]. However, in practical IB materials N_I depends on the technological approach used in the fabrication. In particular, for IB materials based on QDs, N_I is expected to be around $10^{15} - 10^{16} \text{ cm}^{-3}$ [Aka 98, Aka 02], similar to the dopant impurity concentration, and for IB materials based on HMAs and DLs, N_I is expected to be around $10^{20} - 10^{21} \text{ cm}^{-3}$ [Olea'08; Wang'09b], significantly above typical dopant impurity concentrations. In order to guarantee the IB operating principles, a portion of the IB-states must be occupied by electrons (n_I) and the rest must be empty, which is to say, occupied by holes (p_I), so that $N_I = p_I + n_I$. How the occupation of these states impacts on the result of CV measurements can be studied using analytical models similar to that reported in [Luque'06b]. Below, we explain the model used. This model includes the charge density associated to the IB (Q_{IB}), which depends on the number of acceptor-states and donor-states that form the IB per unit of volume (N_{AIB} and N_{DIB} respectively) and the concentration of IB-electrons and IB-holes (n_I and p_I respectively). Since these parameters are related through two conditions, $N_{AIB} + N_{DIB} = N_I$ and $n_I + p_I = N_I$, Q_{IB} can be expressed in terms of any two independent parameters, for example $Q_{IB}(N_{DIB}, n_I) = e(N_{DIB} - n_I)$. Equation (5.3) provides the charge density at any point of an IB material:

$$\rho = e(p - n + N_D^+ - N_A^- + N_{DIB} - n_I) \quad (5.3)$$

To calculate the charge density we need to determine the value of each element of equation (5.3) using the following expressions [Luque'06b]:

$$n(\phi) = n_i \exp\left(\frac{\varepsilon_{Fe} - E_i^0 + e\phi}{k_B T}\right) \quad (5.4)$$

$$p(\phi) = n_i \exp\left(\frac{E_i^0 - \varepsilon_{Fh} - e\phi}{k_B T}\right) \quad (5.5)$$

$$n_l(\phi) = \frac{N_l [\sigma_h n_i \exp[(E_i^0 - E_{IB}^0)/k_B T] - \sigma_n n(\phi)]}{\sigma_n n_i \exp\left[\frac{(E_{IB}^0 - E_i^0)}{k_B T}\right] + \sigma_p n_i \exp\left[\frac{(E_i^0 - E_{IB}^0)}{k_B T}\right] + \sigma_p p(\phi) + \sigma_n n(\phi)} \quad (5.6)$$

where n_i is the intrinsic concentration, E_i^0 is the intrinsic level, E_{IB}^0 is the IB energy and σ_n and σ_p are electron and hole capture cross sections respectively. ϕ is the electrostatic potential, whose value varies from 0 to $V = V_{bi} + V_r$, so that different values of ϕ lead to different values of ρ . The solutions of ρ must fulfill $\rho(\phi = V_{bi} + V_r) = 0$ and $\varepsilon_{Fe} - \varepsilon_{Fh} = -eV_r$, where ε_{Fe} and ε_{Fh} are the quasi Fermi levels of electrons and holes respectively.

Once we know $\rho(\phi)$ we can obtain the electric field ($\mathcal{E}$) by using the Poisson's equation [Luque'06b].

$$\frac{d^2 \phi}{dx^2} = -\frac{1}{\varepsilon_s} \rho(x) \quad (5.7)$$

$$\mathcal{E}(\phi) = -\frac{d\phi}{dx} = [\mathcal{E}_0^2 - \frac{2}{\varepsilon_s} \int_0^\phi \rho(\phi') d\phi']^{1/2} \quad (5.8)$$

where ε_s is the permittivity of the semiconductor and $\mathcal{E}_0$ is the surface electric field across the plane $x = 0$, where $\phi = 0$. We can also determine the position x that correspond to every value of ϕ by means of the following expression:

$$x = -\int_0^\phi [1/\mathcal{E}(\phi')] d\phi' \quad (5.9)$$

From this model it is possible to obtain $\mathcal{E}_0$ as a function of V_r , so applying Gauss' theorem we can also obtain the corresponding total space charge Q (per unit area of the device):

$$\mathcal{E}_0 = -\frac{1}{\varepsilon_s} Q \quad (5.10)$$

Finally, the theoretical CV characteristics can be obtained by calculating the small-signal capacitance of a device with area A for different V_r :

$$C = A \frac{\Delta Q}{\Delta V_r} \quad (5.11)$$

Fig. 5.2 shows the simulated CV curve for a 1 cm^2 Schottky diode based on an IB material. The IB is located at 0.3 eV from the CB of the GaAs host semiconductor and it is

formed by $N_I/2$ acceptor-states and $N_I/2$ donor-states, being $N_I = 8 \cdot 10^{16} \text{ cm}^{-3}$. Data are obtained assuming $V_{bi} = 0.7 \text{ eV}$ and two different doping levels, $N_D = 4 \cdot 10^{16} \text{ cm}^{-3}$ and $N_D = 1 \cdot 10^{16} \text{ cm}^{-3}$. These data and the remaining parameters, σ_n and σ_p , are similar to data estimated from experimental results obtained in InAs/GaAs QDs [Luque'06b].

Fig. 5.2: Simulated CV curve for a 1 cm^2 Schottky diode based on an IB material. The value of N_{SCR} obtained from the slope of the curve is greater than the value of N_D . The V_{bi} obtained from the intersection of the curve is similar to the theoretical value (0.7 V).

The CV curves of Fig. 5.2 are obtained for $T = 300\text{K}$. These CV curves evidence that, for a material with an IB formed by $N_I/2$ acceptor-states and $N_I/2$ donor-states, the N_{SCR} obtained does not approximate N_D but is closer to $N_D + N_I/2$. This result is independent of whether the IB-sates are localized or de-localized, and it must be taken into account when CV measurements of IB materials are analyzed.

5.2.2 Deep level transient spectroscopy (DLTS)

The DLTS technique can provide information about energy levels that act as carrier traps inside the SCR, such as their relative position with respect to the CB and the VB, their concentration and their capture cross section [Lang'74]. However, these parameters can be determined only when the charge state of the traps under study can be significantly modulated. For this reason, first of all, we will analyze the electron occupancy of carrier traps in Section 5.2.2.a.

5.2.2.a Electron occupancy of carrier traps

In a conventional semiconductor with a trap density N_T (per unit of volume), we can define n_T as the density of traps occupied by electrons and p_T as the density of traps occupied by holes, so that $N_T = n_T + p_T$ regardless whether traps are acceptors or donors.

The occupancy of the N_T traps is determined by the emission and capture processes depicted in Fig. 5.1, so that [Schroder'06]:

$$\frac{dn_T}{dt} = \frac{dp}{dt} - \frac{dn}{dt} = (c_n n + e_p)(N_T - n_T) - (e_n + c_p p)n_T \quad (5.12)$$

and in the steady state ($\frac{dn_T}{dt} = 0$):

$$n_T = \frac{c_n n + e_p}{c_n n + e_p + e_n + c_p p} N_T \quad (5.13)$$

These equations evidence that the occupation of traps and its temporal evolution depends on the value of n and p , which clearly vary along the structure of a Schottky diode or a p-n junction. In the case of a conventional Schottky contact on a n-type semiconductor (p can be neglected) two situations can simplify the solution of n_T [Schroder'06]:

- (1) Capture dominates emission $c_n n \gg e_n, e_p$: In equilibrium this condition is valid when the Fermi level ε_F is above the energy of the traps E_T [Blood'92c], leading to:

$$n_T = \frac{c_n n + e_p}{c_n n + e_p + e_n} N_T \approx N_T \quad (5.14)$$

- (2) Emission dominates capture $c_n n \ll e_n, e_p$: In equilibrium this condition is valid when the Fermi level ε_F is below the energy of the traps E_T [Blood'92c], leading to:

$$n_T = \frac{e_p}{e_p + e_n} N_T \quad (5.15)$$

In case (2) the value of n_T depends on the relation between e_n and e_p . This relation is defined by the relative position of the trap levels inside the bandgap of the semiconductor, so that, in general, $e_n \gg e_p$ for traps located above the mid-gap and $e_n \ll e_p$ for traps located below the mid-gap [Blood'92c]. Traps with $e_n \gg e_p$ interact mostly with the CB and receive the name of electron-traps, while traps with $e_n \ll e_p$ interact mostly with the VB and receive the name of hole-traps, regardless of whether the traps are acceptor-levels or donor-levels. These two kinds of carrier traps are illustrated in Fig. 5.3 (a) and Fig. 5.3 (b) respectively. Fig. 5.3 (a) shows that in the n-type semiconductor of a Schottky diode, electron-traps located inside the neutral region are practically full of electrons ($n_T \approx N_T$) since in this region capture dominates emission, and

electron-traps located inside the SCR are practically empty of electrons ($n_T \approx 0$) since in this region emission dominates capture. Likewise, Fig. 5.3 (b) shows that in the p-type semiconductor of a Schottky diode, hole-traps located inside the neutral region are practically empty of electrons ($n_T \approx 0$) since in this region emission dominates capture, and hole-traps located inside the SCR are practically full of electrons ($n_T \approx N_T$) since in this region capture dominates emission.

Fig. 5.3: (a) Band diagram of a Schottky diode based on a n-type semiconductor with electron-traps for $V_r = 0V$ (top) and $V_r > 0V$ (bottom). (b) Band diagram of a Schottky diode based on a p-type semiconductor with hole-traps for $V_r = 0V$ (top) and $V_r > 0V$ (bottom). In these figures the electron occupancy of electron-traps is determined by ϵ_{Fe} and the electron occupancy of hole-traps is determined by ϵ_{Fh} . These quasi-Fermi levels are equal under equilibrium. Carrier traps placed between vertical red lines change their occupancy significantly.

Since, the charge state of trap levels depends on the relative position of ϵ_F with respect to E_T [Blood'92c], this charge state can be modified by varying the position of ϵ_F . In Schottky diodes and p-n junctions this can be done by applying different bias voltage, as illustrated in Fig. 5.3. In this figure it can be observed that the traps located within the vertical red lines under equilibrium ($V_r = 0$) change their charge state when a reverse voltage is applied ($V_r > 0$). In particular, for electron-traps ($e_n \gg e_p$) located close to the SCR edge of a n-type semiconductor (Fig. 5.3a), $n_T \approx N_T$ when $V_r = 0$ and $n_T \approx 0$ when $V_r > 0$. The temporal evolution of these traps from $n_T \approx N_T$ to $n_T \approx 0$ is obtained by solving equation (5.12). If we consider that in $t = 0$ devices are biased from zero to

reverse voltage and mobile carriers (n and p) are swept out of the SCR, we obtain [Schroder'06]:

$$n_T(t) = n_T(0) \cdot \exp(-e_n t) \approx N_T \cdot \exp(-e_n t) \quad (5.16)$$

equation (5.16) is also valid for hole-traps ($e_n \ll e_p$) close to the SCR edge of a p-type semiconductor (Fig. 5.3b) by replacing n_T by p_T and e_n by e_p [Blood'92c].

$$p_T(t) = p_T(0) \cdot \exp(-e_p t) \approx N_T \cdot \exp(-e_p t) \quad (5.17)$$

Equations (5.16) and (5.17) describe the temporal evolution of electron-traps and hole-traps respectively when emission dominates capture, regardless of whether traps are acceptor-levels or donor-levels. These equations consider that, previous to the emission process, electron-traps and hole-traps are full of electrons and holes respectively.

5.2.2.b Capacitance transients

The way in which the charge state of traps impacts on the $N_{SCR}(x \rightarrow x_{SCR})$ of Schottky diodes and abrupt asymmetric p-n junctions depends on whether traps are acceptor-levels or donor-levels [Blood'92b]. For example, for electron-traps close to the SCR edge of n-type semiconductors and hole-traps close to the SCR edge of p-type semiconductors, termed majority carrier traps, four possible combinations are possible when suddenly emission dominates capture:

- (1) Electron-traps formed by acceptor-levels,

$$N_{SCR}(t) = N_D^+ - n_T(t); N_{SCR}(0) = N_D^+ - N_T; N_{SCR}(\infty) = N_D^+$$

- (2) Electron-traps formed by donor-levels:

$$N_{SCR}(t) = N_D^+ + N_T - n_T(t); N_{SCR}(0) = N_D^+; N_{SCR}(\infty) = N_D^+ + N_T$$

- (3) Hole-traps formed by acceptor-levels,

$$N_{SCR}(t) = N_A^- + N_T - p_T(t); N_{SCR}(0) = N_A^-; N_{SCR}(\infty) = N_A^- + N_T$$

- (4) Hole-traps formed by donor-levels:

$$N_{SCR}(t) = N_A^- - p_T(t); N_{SCR}(0) = N_A^- - N_T; N_{SCR}(\infty) = N_A^-$$

The analysis of cases (1)-(4) reveals that $N_{SCR}(x \rightarrow x_{SCR})$ increases with time when there is a net emission of majority carriers from traps. Note that this effect does not depend on whether the traps are donor-levels or acceptor-levels. The only difference between donor and acceptors is in the value of N_{SCR} [Blood'92c]. The capacitance of Schottky diodes and abrupt asymmetric p-n junctions depends on the N_{SCR} at the

depletion region edge, $N_{\text{SCR}}(x \rightarrow x_{\text{SCR}})$. As a consequence, an increasing capacitance transient appears when there is a net emission of majority carriers from traps. This increasing capacitance transient follows the dependence of equation (5.18) [Schroder'06].

$$C(t) = A \sqrt{\frac{\epsilon \epsilon_0 e}{2(V_{\text{bi}} + V_{\text{r}})}} \cdot \sqrt{N_{\text{SCR}}(t)} \approx A \sqrt{\frac{\epsilon \epsilon_0 e N_{\text{D}}}{2(V_{\text{bi}} + V_{\text{r}})}} \cdot \sqrt{1 - \frac{n_{\text{T}}(t)}{N_{\text{D}}}} = C_0 \sqrt{1 - \frac{n_{\text{T}}(t)}{N_{\text{D}}}} \quad (5.18)$$

This equation is valid for n-type semiconductors with electron-traps formed by acceptor-levels and it is also valid for donor-levels by replacing N_{D} by $N_{\text{D}} + N_{\text{T}}$. In the case of p-type semiconductors with hole-traps, equation (5.18) can be also used by replacing N_{D} by N_{A} and n_{T} by p_{T} .

For electron-traps close to the SCR edge of p-type semiconductors and hole-traps close to the SCR edge of n-type semiconductors, termed minority carrier traps, four possible combinations are possible when suddenly emission dominates capture:

(5) Electron-traps formed by acceptor-levels,

$$N_{\text{SCR}}(t) = N_{\text{A}}^- + n_{\text{T}}(t); N_{\text{SCR}}(0) = N_{\text{A}}^- + N_{\text{T}}; N_{\text{SCR}}(\infty) = N_{\text{A}}^-$$

(6) Electron-traps formed by donor-levels:

$$N_{\text{SCR}}(t) = N_{\text{A}}^- - N_{\text{T}} + n_{\text{T}}(t); N_{\text{SCR}}(0) = N_{\text{A}}^-; N_{\text{SCR}}(\infty) = N_{\text{A}}^- - N_{\text{T}}$$

(7) Hole-traps formed by acceptor-levels,

$$N_{\text{SCR}}(t) = N_{\text{D}}^+ - N_{\text{T}} + p_{\text{T}}(t); N_{\text{SCR}}(0) = N_{\text{D}}^+; N_{\text{SCR}}(\infty) = N_{\text{D}}^+ - N_{\text{T}}$$

(8) Hole-traps formed by donor-levels:

$$N_{\text{SCR}}(t) = N_{\text{D}}^+ + p_{\text{T}}(t); N_{\text{SCR}}(0) = N_{\text{D}}^+ + N_{\text{T}}; N_{\text{SCR}}(\infty) = N_{\text{D}}^+$$

The analysis of cases (5)-(8) reveals that $N_{\text{SCR}}(x \rightarrow x_{\text{SCR}})$ decreases with time when there is a net emission of minority carriers from traps, regardless of whether traps are acceptor-levels or donor-levels [Blood'92c]. As a consequence, a decreasing capacitance transient appears when there is a net emission of minority carriers from traps. This decreasing capacitance transient follows the dependence of equation (5.19) [Schroder'06].

$$C(t) = A \sqrt{\frac{\epsilon \epsilon_0 e}{2(V_{\text{bi}} + V_{\text{r}})}} \cdot \sqrt{N_{\text{SCR}}(t)} \approx A \sqrt{\frac{\epsilon \epsilon_0 e N_{\text{D}}}{2(V_{\text{bi}} + V_{\text{r}})}} \cdot \sqrt{1 + \frac{p_{\text{T}}(t)}{N_{\text{D}}}} = C_0 \sqrt{1 + \frac{p_{\text{T}}(t)}{N_{\text{D}}}} \quad (5.19)$$

This equation is valid for n-type semiconductors with hole-traps formed by donor-levels and it is also valid for acceptor-levels by replacing N_{D} by $N_{\text{D}} - N_{\text{T}}$. In the case of p-

type semiconductors with electron-traps, equation (5.19) can be also used by replacing N_D by N_A and p_T by n_T .

In order to observe capacitive transients associated to carrier emission, it is necessary that carriers are previously captured. This is taken into account in cases (1)-(8) under the condition that electron-traps and hole-traps are full of electrons and holes respectively at $t = 0$. The efficiency of capture processes depends on the relative position between traps and the quasi-Fermi that describes the electron occupancy of these traps [Blood'92c]. Each energy level has its own quasi-Fermi level [Martí'04], but it has usually been considered that the quasi-Fermi level of energy levels inside the bandgap matches with the quasi-Fermi level that describe the electron occupancy of the CB or with the quasi-Fermi level that describe the hole occupancy of the VB. In particular, since electron-traps interact mostly with the CB, it can be considered that their quasi-Fermi level approximates to ε_{Fe} . In the same way, since hole-traps interact mostly with the VB, it can be considered that their quasi-Fermi level approximates to ε_{Fh} . As a consequence, an efficient capture of electrons by electron-traps takes place when ε_{Fe} is above the energy of electron-traps and an efficient capture of holes by hole-traps takes place when ε_{Fh} is below the energy of hole-traps. In the case of minority carrier traps, these conditions can be fulfilled by means of applying forward voltages to Schottky diodes and p-n junctions [Schroder'06]. This is illustrated in Fig. 5.4, where we represent the typical voltage bias used to force the capture and emission of majority and minority carriers from traps and the corresponding capacitance transients.

Fig. 5.4: Sketch of the typical voltage pulses used to force the capture and emission of majority carriers (left) and minority carriers (right) from traps. In this diagram positive values of V correspond to forward biases and negative values of V correspond to reverse biases. For $t > t_1$ net emission of carriers from traps takes place. If these carriers are majority carriers, the emission leads to an increasing capacitance transient, but if they are minority carriers, the emission leads a decreasing capacitance transient. In this diagram t is not to scale, since

in practice $t_0 \approx t_1$ is considered.

As can be seen in Fig. 5.4, the capacitance transient can be divided in two parts:

- The capacitance transient from $t = t_0$ to $t = t_1$, which corresponds to a variation of V_r . The duration of this transient is related with the time necessary for mobile carriers to be swept out of the SCR, which is around tens of picoseconds [Kuoppa'07].
- The capacitance transient from $t > t_1$, which corresponds to the variation of N_{SCR} with time. The duration of this transient depends on the time necessary for electrons to be emitted from electron-traps to the CB and holes to be emitted from hole-traps to the VB, which typically is around $10^{-6} - 10^{-3}$ seconds [Kuoppa'07].

The sampling time of typical capacitance meters is much greater than picoseconds, so capacitance transients from $t = 0$ to $t = t_1$ are not detected with these meters. For this reason, hereinafter, we will considered $t_0 \approx t_1 = 0$.

5.2.2.c DLTS measurements

The DLTS technique has been used to study conventional semiconductors, in which trap concentrations are usually below doping concentrations. Under this condition, the capacitance transient that results from combining equations (5.16) and (5.18), for the case of n-type semiconductors with electron-traps formed by acceptor-levels, can be approximated to [Schroder'06]:

$$C(t) = C_0 \sqrt{1 - \frac{n_T(t)}{N_D}} \approx C_0 \left(1 - \frac{n_T(t)}{2N_D}\right) \approx C_0 \left(1 - \frac{N_T \cdot \exp(-e_n t)}{2N_D}\right) \quad (5.20)$$

According to equation (5.20), the capacitance follows an exponential dependence with time determined by e_n , which is the emission rate of electrons from traps. In equilibrium, it is possible to relate this parameter with the relative position of traps with respect to the CB ($E_C - E_T$) and their capture cross section (σ_n) by means of the principle of detailed balance [Blood'92c]. This principle states that the emission of electrons (process 2 in Fig. 5.1) and the inverse capture of electrons (process 3 in Fig. 5.1) must balance in equilibrium, so that [Blood'92c]:

$$e_{n0} n_{T0} = c_{n0} n_0 (N_T - n_{T0}) \quad (5.21)$$

where the subscript 0 stands for equilibrium. The capture coefficient c_{n0} is defined by $c_{n0} = \sigma_{n0} v_{th}$ [Schroder'06], being v_{th} the thermal velocity of electrons and σ_{n0} the capture cross section of electrons. Including this definition in equation (5.21) leads to:

$$e_{n0} = \sigma_{n0} v_{th} N_C \exp\left(-\frac{E_C - E_T}{k_B T}\right) \quad (5.22)$$

where N_C is the effective density of CB-states. Strictly, equation (5.22) is only valid in thermal equilibrium. However, this equation is commonly used also out of equilibrium. In equation (5.22) we must include the temperature dependence of parameters, such as $v_{th} \propto T^{1/2}$ and $N_C \propto T^{3/2}$. To introduce the temperature dependence of $E_C(T) - E_T(T)$ we can use the definition of the energy level of a trap as the change in chemical potential required for the formation of a free carrier and an ionized trap. At constant temperature and pressure, the change in chemical potential is defined as the increase in Gibbs free energy, so $\Delta G(T) = E_C(T) - E_T(T)$ [Blood'92d]. The change in Gibbs free energy $\Delta G(T)$ is related to changes in enthalpy (ΔH) and entropy (ΔS), so

$$\Delta G(T) = \Delta H - T\Delta S \quad (5.23)$$

In equation (5.23) the value of ΔS arises from changes in electronic and vibronic configurations. If in this equation we remove the temperature dependence of $v_{th}(T)$ and $N_C(T)$ by plotting the logarithm of $(e_n \cdot T^{-2})$ as a function of T^{-1} , we obtain the Arrhenius plot described by equation (5.24) [Blood'92d].

$$e_n \cdot T^{-2} = \gamma \sigma_n \exp\left(\frac{\Delta S}{k_B}\right) \exp\left(-\frac{\Delta H}{k_B T}\right) \quad (5.24)$$

For a specific material with a known γ , we can obtain ΔH from the slope of the Arrhenius plot and the apparent capture cross section, $\sigma_n \exp\left(\frac{\Delta S}{k_B}\right)$, from its interception. Note that in this analysis we have considered σ_n as independent of temperature, which does not necessarily have to be true, especially for traps in III-V semiconductors [Blood'92d].

The objective of the DLTS technique is to obtain the Arrhenius plot described by equation (5.24) by determining the emission rate of electrons (or holes) at different temperatures. With this technique the emission rates are determined by measuring the capacitance transient that appear after applying a reverse voltage that force the emission of carriers from traps [Lang'74]. According to equation (5.20), this capacitance transient follows an exponential dependence with time so, for two different times t_1 and t_2 :

$$C(t_2) - C(t_1) \approx C_0 \frac{N_T}{2N_D} [\exp(-e_n t_1) - \exp(-e_n t_2)] \quad (5.25)$$

The capacitance variation of equation (5.25), $\Delta C = C(t_2) - C(t_1)$, is maximal when $e_n = \frac{\ln(t_2/t_1)}{(t_2 - t_1)}$ [Lang'74]. This fact is used by the DLTS technique to obtain the corresponding e_n for different T from two types of DLTS diagrams:

- Diagrams that represent ΔC as a function of T . In these diagrams t_1 and t_2 are fixed and define a window rate, $WR = \frac{\ln(t_2/t_1)}{(t_2-t_1)}$, so that when ΔC is maximum, e_n corresponds to WR for the temperature associated to the peak of ΔC . Different pairs of data (e_n, T) are obtained by using different WR . An illustrative diagram is represented in Fig. 5.5.

Fig. 5.5: Illustration of the construction of a DLTS diagram from the capacitance transients at different temperatures. (after [Lang'74])

- Diagrams that represent ΔC as a function of the window rate, $WR = \frac{\ln(t_2/t_1)}{(t_2-t_1)}$. In these diagrams the temperature T is constant and the WR associated to the maximum ΔC corresponds to e_n . Different pairs of data (e_n, T) are obtained by using different temperatures.

From these diagrams we can obtain the Arrhenius plot of equation (5.24), and therefore, we can obtain ΔH and the apparent capture cross section, $\sigma_n \exp\left(\frac{\Delta S}{k_B}\right)$, associated to carrier traps. An additional parameter, the concentration of carrier traps (N_T), can be determined from the following expression [Schroder'06]:

$$C(\infty) - C(0) \approx C_0 \frac{N_T}{2N_D} \quad (5.26)$$

assuming N_D is known.

In this Section we have only analyzed the case of n-type semiconductors with electron-traps, but similar results are obtained for the other kind of majority carrier traps, hole-traps in p-type semiconductors, and also for minority carrier traps. The main difference is that, while majority carrier traps lead to increasing capacitance transient and positive ΔC (for $t_2 > t_1$), minority carrier traps lead to decreasing capacitance transient and negative ΔC .

5.2.2.d DLTS measurements in IB materials

An ideal IB is formed by energy states with de-localized wave functions. A priori, this characteristic of IB-states makes it possible that, after applying a reverse voltage, carriers in the IB may behave as mobile carriers and be swept out the SCR by drift, instead of being thermally emitted from the IB. If that were the case, the DLTS technique could not be used to study the characteristics of IB because equation (5.12) would not be valid (this equation is only valid when there is not transport through the IB). However, as mentioned in Section 1.1.3, IB-carriers do not have to exhibit a high mobility [Martí'12]. The mobility of IB-carriers depends on the IB-bandwidth, so that for the limiting case of an IB with zero-bandwidth, carriers have zero mobility regardless their wave functions [Martí'12]. For this reason we must not discard the application of the DLTS technique to IB materials, especially when the IB material is based on QDs since in this case the IB-carriers have low mobility as a consequence of their confinement inside the QDs (if tunneling transfer is not produced between QDs [Antolín'10]).

An ideal IB is closer to the CB or the VB. This distribution makes possible for IB-states to behave as electron-traps ($e_n \gg e_p$) or hole-traps ($e_n \ll e_p$). As in the case of conventional carrier traps, the electron occupancy of IB-states in steady state (n_l) is determined by equation (5.13). This occupancy can be expressed in terms of the quasi Fermi level of the IB, ε_{FIB} . In ideal IB materials ε_{FIB} should be located inside the IB to guarantee the partial electron filling of the IB (explained in Section 1.1.3). However, this condition is not fulfilled when the IB is placed inside the SCR of Schottky diodes or p-n junctions [Martí'08], as illustrated in Fig. 5.6 (a). The band diagrams of Fig. 5.6 are obtained using the mathematical model detailed in Section 5.2.1.a and the same data as those used to simulate one of the CV curves of Fig. 5.2: a 1 cm² Schottky diode based on GaAs doped with $N_D = 4 \cdot 10^{16} \text{ cm}^{-3}$ and a built-in voltage $V_{\text{bi}} = 0.7 \text{ eV}$. The IB is located at 0.3 eV from the CB, and it is characterized by a zero-bandwidth, $N_l = 8 \cdot 10^{16} \text{ cm}^{-3}$ ($N_l/2$ acceptor-states and $N_l/2$ donor-states), $\sigma_n = 2.35 \cdot 10^{-12} \text{ cm}^2$ and $\sigma_p = 3 \cdot 10^{-14} \text{ cm}^2$ [Luque'06b].

Fig. 5.6: (a) Band diagram of a 1 cm^2 Schottky diode based on an IB material doped with $N_D = 4 \cdot 10^{16} \text{ cm}^{-3}$. The IB is located at 0.3 eV from the CB, $N_I = 8 \cdot 10^{16} \text{ cm}^{-3}$ ($N_I/2$ acceptor-states and $N_I/2$ donor-states), $\sigma_n = 2.35 \cdot 10^{-12} \text{ cm}^2$ and $\sigma_p = 3 \cdot 10^{-14} \text{ cm}^2$. These diagrams are obtained for two reverse voltages $V_r = 0\text{V}$ and $V_r = 2\text{V}$. (b) Variation of n_l along the structure of a Schottky diode for these reverse voltages.

Fig. 5.6 (a) illustrates that, in the neutral region of an IB material with the features mentioned above, ε_{FIB} is not located inside the IB but is located above it. This is because in IB materials with $N_I/2$ acceptor-states, $N_I/2$ donor-states and $N_D = 0.5N_I$, the charge neutrality ($\rho = 0$) is obtained when IB-states are almost full of electrons, $n_l = 7.6 \cdot 10^{16} \text{ cm}^{-3} = 0.95N_I$. Different IB materials with different features lead to different electron-occupancies for the IB-states placed in the neutral region. For example, in IB material with $N_I/2$ acceptor-states, $N_I/2$ donor-states and $N_D \ll N_I$, the charge neutrality is obtained for $n_l \approx 0.5 \cdot N_I$. The same result is obtained in IB materials with N_I acceptor-states and $N_D = 0.5N_I$. In these two material families, ε_{FIB} is located inside the IB in the neutral region. However, for IB materials with N_I acceptor-states and $N_D \ll N_I$, the charge neutrality is obtained when $n_l \approx 0$ and ε_{FIB} is located below the IB.

From this analysis we conclude that the variation of n_l along the structure of Schottky diodes (Fig. 5.6b) varies from case to case. In general, $n_l \approx 0$ in the SCR and $n_l = f \cdot N_I$ in the neutral region (being $0 \leq f \leq 1$), so that the IB-states located close to the SCR edge under equilibrium (delimited by red lines in Fig. 5.6) can change their charge

state when a reverse voltage is applied, from $n_i = f \cdot N_i$ to $n_i \approx 0$. The temporal evolution of these IB-states can be obtained by solving equation (5.12), considering that in $t = 0$ devices are biased from zero to reverse voltage:

$$n_i(t) = n_i(0) \cdot \exp(-e_n t) \quad (5.27)$$

Equation (5.27) is valid for IB-states that behave as electron-traps ($e_n \gg e_p$) and also for IB-states that behave as hole-traps ($e_n \ll e_p$) by replacing n_i by p_i and e_n by e_p . This equation is similar to equation (5.16) used for conventional electron-traps, except that in this case the value of $n_i(0)$ ($n_i(0) = f \cdot N_i$) depends on the features of the IB materials, in terms of the acceptor-nature or the donor-nature of IB- states and the value of N_D .

The temporal evolution of IB-states impacts on the net charge density of the SCR of Schottky diodes and abrupt asymmetric p-n junctions (N_{SCR}) as described in Section 5.2.2.b. In that Section it is concluded that, regardless of the nature of the IB-states, the emission of majority carriers inside the SCR increases the value of N_{SCR} at the depletion region edge, producing an increasing capacitance transient. In an equivalent manner, a decreasing capacitance transient appears when there is a net emission of minority carriers from IB-states. These capacitance transients are described by equations (5.18) and (5.19), which are valid for IB materials except that N_{SCR} does not necessarily need to equal N_D . In IB materials the value of N_{SCR} can be increased by a factor of N_i , depending on the portion of IB-states with acceptor-nature and the portion of IB-states with donor-nature (Section 5.2.1.a).

In general, in IB materials we cannot guarantee that $n_i(0) \ll N_{SCR}$ (or $p_i(0) \ll N_{SCR}$), so in equation (5.20), capacitance must be replaced by the square of the capacitance to obtain an exponential dependence with time [Blood'92e].

$$C^2(t) = C_0^2 \left(1 - \frac{n_i(t)}{N_{SCR}} \right) = C_0^2 \left(1 - \frac{n_i(0) \cdot \exp(-e_n t)}{N_{SCR}} \right) \quad (5.28)$$

Equation (5.28) is valid for n-type semiconductors with IB-states that behave as electron-traps. In the case of p-type semiconductors with IB-states that behave as hole-traps, this equation can be also used by replacing n_i by p_i . According to equation (5.28), if we want to use the DLTS technique to obtain the Arrhenius plot of IB-states, we have to determine the emission rate of electrons (or holes) from the transient of the square of the capacitance. Therefore, the DLTS diagrams for IB materials should represent $\Delta(C^2)$ versus T , or $\Delta(C^2)$ versus WR instead of just ΔC . Note that this is only required when $n_i(0) \ll N_{SCR}$ (or $p_i(0) \ll N_{SCR}$) is not fulfilled, otherwise, conventional DLTS diagrams can be used.

Finally, it is worth emphasizing that equation (5.22) can be used in IB materials if ε_{FIB} matches the quasi-Fermi level of the energy band that receives the carriers emitted

(ε_{Fe} in the case of electron-emission and ε_{Fh} in the case of hole-emission). In general this is not true and equation (5.22) should be replaced by equation (5.29):

$$e_{n0} = \sigma_{n0} v_{th} N_C \exp\left(-\frac{E_C - E_T + \varepsilon_{FIB} - \varepsilon_{Fe}}{k_B T}\right) \quad (5.29)$$

Equation (5.29) leads to an Arrhenius plot different to the one obtained from equation (5.22). In this new Arrhenius plot, the slope is $\Delta H + \varepsilon_{FIB} - \varepsilon_{Fe}$, which can make it even more difficult to determine the position of the IB inside the bandgap. However, according to Fig. 5.6 (a), ε_{FIB} equals ε_{Fe} for the IB-states within the dashed vertical red lines, which are the ones studied with the DLTS technique.

In summary, the DLTS technique can be used to study IB materials because the theory behind this technique is valid for IB-states and not only for conventional carrier traps. The only difference is that the Arrhenius plot and the corresponding ΔH and apparent capture cross section are obtained by DLTS diagrams that must represent $\Delta(C^2)$ instead of ΔC if the condition $n_I(0) \ll N_{SCR}$ (or $p_I(0) \ll N_{SCR}$) is not fulfilled. Besides, it can be no possible to determine the value of N_I in IB materials if the features of the material under study lead to $n_I(0) < N_I$.

5.3 Experimental set-up for DLTS measurements

The DLTS system implemented during this Thesis resembles a conventional DLTS system with additional characteristics that are required to characterize IBSCs, such as the possibility of measuring $\Delta(C^2)$ instead of ΔC if the condition $n_I(0) \ll N_{SCR}$ (or $p_I(0) \ll N_{SCR}$) is not fulfilled. The implemented DLTS system allows fast data acquisition and simultaneous mathematical processing by means of software and hardware automation. We will begin this Section with the description of the elements of the experimental set-up and the measurement procedure, to finalize explaining what can make the measuring unfeasible. This information may then be useful for any reader undertaking the task of implementing a conventional DLTS system or a DLTS system adapted to IBSCs.

5.3.1 Description of the experimental set-up and the measurements procedure

Each element of the experimental DLTS set-up depicted in Fig. 5.7 has a specific objective: to control the temperature of the devices under study, to control the voltage bias applied to devices, to measure and acquire the capacitance signal of devices, or to process the capacitance signal and to provide DLTS diagrams.

Fig. 5.7: Sketch of the DLTS system implemented at IES-UPM.

Two elements are used to control the temperature of the devices: liquid nitrogen to cool the holder of the samples and a “LAKESHORE 330 temperature controller” to heat the holder by means of the power dissipated by a rheostat. This power is calculated in function of the actual temperature (measured with a PT-100 Platinum sensor) and the desired control temperature, or set-point. While the power dissipated by the rheostat is variable, the cooling rate is practically constant. This rate is regulated by a motor pump that forces the liquid nitrogen to rise until reaching the back surface of the holder. Since during the DLTS measurements the device temperature can reach very low values (down to 77 K), it is necessary to place the device inside a vacuum chamber to avoid water condensation.

The element in charge of controlling the voltage bias applied to the devices is a “TEKTRONIX AFG 3022B dual function generator”. This generator provides voltage pulses with a specific periodicity. The voltage provided by this generator alternates between a minimum and a maximum value, in a time scale that can be considered instantaneous. If this pulse is applied to the positive terminal of the device, the duration of the maximum voltage can be shorter than the duration of the minimum voltage since the net carrier capture that takes place at the maximum voltage is faster than the net carrier emission that takes place at the minimum voltage. The value of the minimum voltage must lead to a reverse bias while the value of the maximum voltage can lead to a reverse bias (to study majority carrier traps) or to a forward bias (also to study minority carrier traps). These voltages, their duration and their periodicity are adjusted to each device, in order to guarantee capture and emission processes take place. The voltage pulses generated by the

“TEKTRONIX AFG 3022B dual function generator” are applied to one of the terminals of the devices through the “BOONTON 7200 capacitance meter”, using the so-called “External bias” mode.

The main element of the DLTS set-up is the “BOONTON 7200 capacitance meter”, since it measures the transient capacitance signal. The capacitance is measured using a sinusoidal signal of fixed frequency ($\omega = 1\text{MHz}$) and variable amplitude (15-100mV), which is applied to the terminal of the device not connected to the “External bias”. The direct measurement of parallel capacitance (C_p) and the conductance (G) is achieved by using phase sensitive detectors. These measurements can be shown in the display in pF units and S units respectively, or they can be acquired from the rear panel connectors as analog voltage signals. The value of these voltages is limited to between -2V and +2V, and it can be translated to pF and S using proportionality factors that depend on the scale used. To use a specific scale without producing overshoot, it may be necessary to reduce the value of the capacitance and the conductance measured. This can be achieved by using circuits with a tunable capacitance and a tunable conductance which can be subtracted from the capacitance and conductance of the devices under study. Finally, other parameters can be obtained from C_p and G , such as series capacitance (C_s), but only C_p and G can be acquired directly from the rear panel.

$$C_s = C_p - \frac{G^2}{\omega^2 C_p} \quad (5.30)$$

A physical connection interface, a “National Instruments BNC-2110 Connector Block” receives the voltage signals that correspond to C_p and G in order for these analog signals can be acquired by a “PCI DAQ device (NI PCI-6132 S)” located inside the computer of the set-up. The acquisition of these analog signals is triggered by the voltage pulse of the “External bias”, in a manner that the acquisition starts ($t = 0$) when devices become reverse-biased. With the PCI DAQ, analog signals can be acquired with 16-bit precision at sampling rates of up to 3MHz. These features make it possible to reproduce transients $C_p(t)$ and $G(t)$ with suitable accuracy.

Finally, we access the data stored in the PCI DAQ by means of LabVIEW software. Once we obtain C_p and G at a specific sampling rate we can calculate C_s using a MATLAB script inside LabVIEW. The same script can be used to analyze these transients and obtain the DLTS diagrams described in Section 5.2.2.c. To reduce the imprecision of the experimental results, the transients are averaged from measurements repeated under the same experimental conditions, applying the same voltage pulse several times.

If we follow this measurement procedure at different temperatures, we can obtain $\Delta C_p - T$, $\Delta G - T$ and $\Delta C_s - T$ diagrams. These diagrams are especially useful to identify the presence of majority carrier traps from positive peaks and the presence of minority

carrier traps from negative peaks. If we follow the same measurement procedure at fixed temperatures, we can obtain $\Delta C_p - WR$, $\Delta G - WR$ and $\Delta C_s - WR$ diagrams. These diagrams are especially useful to obtain the trap concentration N_T and the Arrhenius plot, and consequently ΔH and the apparent capture cross section, $\sigma_n \exp\left(\frac{\Delta S}{k_B}\right)$. Note that in the case of IB-states, if the condition $n_1(0) \ll N_{SCR}$ (or $p_1(0) \ll N_{SCR}$) is not fulfilled, we have to obtain $\Delta(C^2)$ instead of ΔC , which is possible by using a MATLAB script to calculate C_p^2 , G^2 and C_s^2 .

5.3.2 Constraints of the measurements

The main challenge of the DLTS set-up is obtaining accurate measurements of capacitance and conductance. This can be complicated by the presence of parasitic C introduced by the coaxial cables of the set-up and the electrical package of the samples under study. Fortunately, these parasitic components can be subtracted from the measurements by using the zeroing option of the BOONTON, which must be activated before any measurement.

The measurements of capacitance and conductance can also be impacted by the characteristics of the devices under study. In general, for small-signal voltages, the operation of real devices is not described by circuital models based on a capacitor, due to the presence of series resistances and parallel resistances. The internal circuits of BOONTON are designed to provide the capacitance of capacitors connected in parallel with resistances (C_p). For this reason, the direct measurements obtained with BOONTON can provide, with reasonable accuracy, the capacitance of devices with acceptable quality (high parallel resistances) and negligible series resistances, and the capacitance of devices with poor quality (low parallel resistances) and a zero series resistance. The operation of devices with an acceptable quality and a significant series resistance can be modeled by an equivalent circuit that consists of a capacitor connected in series with a resistance (C_s). This capacitance can be obtained by applying the equation (5.31) to the direct measurements obtained with BOONTON. However, the capacitance of devices with poor quality and series resistances cannot be determined, because their operation is modeled by a capacitor connected in parallel with one resistance and in series with another. These devices usually lead to discrepancies in the results obtained with different scales.

5.4 Experimental results

After we implemented the DLTS system at IES-UPM, we tested the validity of the results obtained. We obtained results that are reproducible according to the requirements

of an ISO-9001:2008 and they are also reproducible with respect to the results obtained with different DLTS systems. In particular, a brief stay research in the University of Aarhus was useful to verify this fact. The most remarkable results obtained with this technique are shown below. These results correspond to conventional solar cells (Section 5.4.1), Schottky contacts on IB materials based on deep levels (DLs) (Section 5.4.2), IBSCs based on highly mismatch alloys (HMAs) (Section 5.4.3) and IBSCs based on QDs (Section 5.4.3).

5.4.1 Experimental results in conventional solar cells

In this Section we analyze the reference solar cells of Section 3.3, in order to study the energy states that emerge inside the bandgap of the GaAs grown at low temperature, responsible of the production of sub-bandgap photocurrent. The results shown in this Section correspond to a solar cell with a structure similar to the one depicted in Fig. 3.13. The structure of this solar cell has an un-doped GaAs layer of 1.5 μm grown at low temperature without Ti, instead of the IB material region. The un-doped GaAs layer should be the less doped one compared to the n-emitter and the p-emitter which have doping levels of $5 \cdot 10^{18} \text{cm}^{-3}$ and $2 \cdot 10^{18} \text{cm}^{-3}$ respectively. For this reason, a priori, the information provided by CV measurements and DLTS measurements should correspond to the GaAs layer grown at low temperature.

The CV measurement of Fig. 5.8 (left) was carried out in dark conditions, biasing the GaAs solar cell from $V_r = 0\text{V}$ to $V_r = 2\text{V}$, at intervals of 0.1V. We measured C_p at different V_r because we assumed that, for small-signal voltages, the device under study operates as a capacitor connected in parallel with a resistance. From these measurements we obtained the distribution of the charge density of the SCR (N_{SCR} vs x_{SCR}) by following the procedure described in Section 5.2.1. This distribution is depicted in Fig. 5.8 (right).

Fig. 5.8: (left) CV measurement at 300 K under the assumption that the device operates as a capacitor connected in parallel with a resistance. (right) Distribution of the charge density at the SCR. In this figure the doping level of the n-emitter and the p-emitter are plotted for comparison.

The data depicted in Fig. 5.8 are obtained assuming that the area of the device is the area of the junction. According to Fig. 5.8 (right), the SCR extends along $\sim 0.9 \mu\text{m}$. This seems to corroborate that, for a V_r in the 0-2V range, the SCR falls inside the GaAs layer grown at low temperature. If this is the case, this layer, which is not doped intentionally, has a doping background that lead to a N_{SCR} of around $5 \cdot 10^{17} \text{ cm}^{-3}$. This charge density, which a priori can be positive or negative, is considerably greater than the expected doping backgrounds (N_B) for GaAs layers grown in MBE reactors at high temperatures ($\sim 600^\circ\text{C}$), which can be as low as 10^{13} cm^{-3} [Chand'89]. However, as we mentioned in Section 5.2.1, the value of N_{SCR} can increase with respect to the value of N_B if carrier traps are inside the SCR. In particular, high point-defect concentrations as high as 10^{20} cm^{-3} have been detected in GaAs layers grown at low temperature [Look'93]. These point-defects have been associated to As anti-sites, which introduce donor-levels inside the GaAs bandgap [Brozel'96]. According to this discussion, the N_{SCR} obtained from CV measurements may correspond to an excessive density of donor-levels introduced by As anti-sites in the GaAs layer grown at low temperature.

In addition to the high N_{SCR} obtained from CV measurements, another unexpected feature obtained from the analysis of these measurements is an incredibly large V_{bi} higher than 146 V. This large V_{bi} is related to the insignificant variation of x_{SCR} for different V_r , from $0.894 \mu\text{m}$ to $0.897 \mu\text{m}$. From this perspective we could think that, in the GaAs solar cell studied in this Section, the SCR extends from the p-emitter to the n-emitter. However,

this is not in agreement with the fact that N_{SCR} is ten times lower than the doping levels of the p-emitter and the n-emitter, and x_{SCR} is narrower than the thickness of the un-doped GaAs layer. In Section 5.4.5 we will detail a possible explanation to this large V_{bi} , caused by effects of mobile carrier tails in p-n junctions.

Fig. 5.9: (a) DLTS diagram obtained by evaluating C_p in $t_1 = 44 \text{ ms}$ and $t_2 = 440 \text{ ms}$ after applying a reverse voltage $V_r = 2 \text{ V}$. In this diagram the positive peaks evidence the presence of majority carrier traps and the negative peaks evidence the presence of minority carrier traps. (b) Arrhenius plot of the carrier traps detected

with the DLTS technique. ΔH and the apparent capture cross section are obtained from the slope and the intersection of the linear fit respectively.

Fig. 5.9 shows the DLTS diagram and the Arrhenius plot obtained with the GaAs solar cell studied in this Section. The DLTS diagram was carried out under dark conditions, using voltage pulses that bias the GaAs solar cell at reverse voltages: at $V_r = 0.5V$ during 50 ms (aimed to force a net capture of carriers by traps) and at $V_r = 2V$ during 450 ms (aimed to force a net emission of carriers from traps). Under these conditions we consider that the operation of the device was modeled by a capacitor connected in parallel with a resistance, so C_p transients were measured by the BOONTON. The DLTS diagram of Fig. 5.9 (a) was obtained from the analysis of the transient produced when the solar cell become biased at $V_r = 2V$ ($t = 0$), for $t_1 = 44ms$ and $t_2 = 440ms$.

The DLTS diagram of Fig. 5.9 (a) shows a positive ΔC_p peak related to majority carrier traps and a negative ΔC_p peak related to minority carrier traps. The detection of these minority carrier traps was unexpected because we only applied reverse voltages to bias the solar cell. According to Section 5.2.2.b, the capture of minority carriers is unlikely under reverse bias conditions because the concentration of these carriers is negligible. However, in abrupt p-n junctions, free-carrier tails can extend into the depletion region of semiconductor junctions, providing minority carrier densities enough high to be detected under reverse voltage conditions [Meijer'83].

The Arrhenius plot of Fig. 5.9 (b) is obtained by analyzing the C_p transients at different temperatures and using different windows rate WR (t_1 and t_2). From this plot we conclude that majority carrier traps have $\Delta H = 0.57eV$ and an apparent capture cross section of $1.2 \cdot 10^{-12}cm^2$, and minority carrier traps have $\Delta H = 0.66eV$ and an apparent capture cross section of $8.4 \cdot 10^{-15}cm^2$. If we assume that the GaAs grown at low temperature is n-type, we can estimate that inside the GaAs bandgap there are electron-traps located at $\sim 0.57eV$ below the CB and hole-traps located at $\sim 0.66eV$ above the VB. These results are in agreement with the results obtained in Section 3.3.1, which indicate that there are energy levels close to the mid-gap of the GaAs grown at low temperature. The features of these energy levels are similar to the features of traps named EL2. These EL2 traps are double donor-levels associated to As anti-sites which can reduce the GaAs absorption threshold to 0.8 eV [Brozel'96].

The features of the carrier traps studied in this Section are obtained under the assumption that N_{SCR} is positive in the GaAs solar cell because it corresponds to donor-levels introduced by As anti-sites. If N_{SCR} were related to other crystalline defects or impurity atoms, this charge density could be negative. If this were the case, the features of the carrier traps would be reciprocal, in other words, hole-traps would be located at $\sim 0.57eV$ below the VB and electron-traps would be located at $\sim 0.66eV$ above the CB.

5.4.2 Experimental results in Schottky contacts on IB materials based on deep levels

In this Section we analyze Schottky diodes based on Si:Ti. The semiconductor structures of these devices were provided by the Universidad Complutense de Madrid. These structures consisted of 300 μm c-Si (111) n-type commercial substrates ($2.2 \cdot 10^{13} \text{cm}^{-3}$) implanted with Ti at high doses (10^{13} , 10^{14} , 10^{15} and 10^{16}cm^{-2}). The implanted surfaces were annealed by PLM with an energy density of $1.4 \text{ J} \cdot \text{cm}^{-2}$. Aluminum contacts were deposited on the implanted surfaces at the IES-UPM to form a Schottky contact. Aluminum contacts were also deposited on the back sides to form, in this case, ohmic contacts. To obtain good ohmic contacts on the bottom, n^+ -layers were fabricated on the back side of the substrates by doping this region with phosphorus atoms. The structure of the devices studied in this Section are depicted in Fig. 5.10 (a).

Fig. 5.10: (a) Structure and expected band diagram of the Schottky diodes based on Si:Ti. (b) SIMS measurements of the Ti depth profile corresponding to substrates implanted with different Ti doses (10^{13} , 10^{14} , 10^{15} and 10^{16}cm^{-2}). The Luque limit is represented as reference by the dashed line (Courtesy of

Dr. David Pastor).

Fig. 5.10 (b) shows the Ti depth profile corresponding to substrates implanted with different implantation doses. In particular, the samples implanted with Ti doses of 10^{15} and 10^{16} cm^{-2} contain Ti concentrations above the Luque limit in the first 20 and 80 nm, and Ti concentrations below the Luque limit at deeper regions. According to [Luque'06a], the non-radiative recombination (NRR) associated to the energy levels introduced by Ti atoms can be inhibited when Ti concentration is above the Luque limit (explained in Section 3.1). This prediction would be confirmed if we measured the capture cross section of the energy levels introduced by different Ti concentrations and we obtained that the value of this parameter decrease significantly for Ti concentrations above the Luque limit. This experiment can be performed using the DLTS technique and the results can complement the results reported in [Antolín'09], where increasing the Ti concentration caused the recovery of the carrier lifetime. In that work the lifetime recovery was associated to the formation of an IB. However, as we mentioned in Section 3.1, in [Krich'12] the authors consider that the lifetime recovery may be associated to variations in the positioning of the energy levels towards shallow positions as the Ti concentration increases. Since the DLTS technique can also provide the relative position of the energy levels inside the bandgap, the experiment proposed here can be useful to conclude whether the lifetime recovery reported in [Antolín'09] is related to the formation of an IB or not.

In this Section we want to use the DLTS technique to scan different positions along the structure of Schottky diodes based on Si:Ti. Of particular interest is the comparison between DLTS measurements corresponding to positions with Ti concentration above the Luque limit and DLTS measurements corresponding to positions with Ti concentration below this limit. Therefore, devices fabricated with Ti doses of 10^{15} and 10^{16} cm^{-2} (corresponding to the blue curve and the purple curve of Fig. 5.10 (b) respectively) are the most suitable to perform DLTS measurements. However, current-voltage measurements evidenced that we only could fabricate rectifier diodes from the substrates implanted with Ti doses of 10^{13} and 10^{14} cm^{-2} (corresponding to the black curve and the red curve of Fig. 5.10 (b) respectively). In these devices the Ti concentration is below the Luque limit at almost every position, which makes these devices unsuitable for the experiment. However, measuring these devices can be useful to study the tendency followed by the capture cross section and the position of the energy levels as the Ti concentration is increased. In particular, the results shown in this Section correspond to a device fabricated with a Ti implanted dose of 10^{13} cm^{-2} . Similar tendencies are obtained with devices fabricated with a Ti implanted dose of 10^{14} cm^{-2} .

Fig. 5.11: (a) Distribution of the charge density of the SCR obtained by CV measurements carried out under the assumption that the device operates as a capacitor connected in series with a resistance. The vertical lines mark the width of the SCR for different reverse voltages: $V_r = 0V$, $V_r = 0.5V$, $V_r = 1V$, $V_r = 1.5V$ and $V_r = 4V$. (b) Comparison with the Ti depth profile obtained from SIMS measurements.

A first batch of CV measurements was carried out assuming that, for small-signal voltages, the device under study operates as a capacitor connected in parallel with a resistance. Measurement of C_p at different V_r revealed an anomalous tendency: C_p

increased when the device was reverse biased from $V_r = 0V$ to $V_r = 1V$. Also, the $C_p - V_r$ curves measured at different frequencies with different LCR equipments (at the University of Aarhus and at ISOM-UPM) showed significant discrepancies. These results suggested that the operation of the device is described by a different circuital model, for example a circuit consisting of a capacitor connected in series with a resistance. This circuital model agrees with the features of the device, which contains almost $300 \mu m$ of c-Si with a very low doping level ($n = 2.2 \cdot 10^{13} cm^{-3}$) and therefore can present a significant series resistance. The validity of this circuital model was confirmed by the agreement of the $C_s - V_r$ curves measured at different frequencies at the ISOM-UPM. From these $C_s - V_r$ curves we obtained the distribution of the charge density of the SCR (N_{SCR} vs x_{SCR}) depicted in Fig. 5.11. In this figure the distribution of N_{SCR} vs x_{SCR} is compared to the Ti depth profile obtained from SIMS measurements.

According to Fig. 5.11, N_{SCR} is around $10^{14} cm^{-3}$ at distances $> 300 nm$ from the implanted surface. This value is above the residual background provided by the substrate provider ($n = 2.2 \cdot 10^{13} cm^{-3}$) and it increases considerably at distances $< 300 nm$ from the implanted surface. Indeed, as we get closer to the implanted surface, N_{SCR} can be as high as $10^{19} cm^{-3}$. The value of N_{SCR} in the first $100 nm$ from the surface fits quite well with the Ti depth profile from SIMS measurements (Fig. 5.11b). This fact indicates that the N_{SCR} obtained from CV measurements may correspond to high concentrations of donor-levels introduced by the presence of high Ti concentrations. If this is the case, it means that: (1) when we bias the sample from $V_r = 0V$ to $V_r = 0.5V$, the SCR extends into a region where the concentration of donor-levels is $10^{19} - 10^{17} cm^{-3}$. (2) When we bias the sample from $V_r = 0.5V$ to $V_r = 1V$, the SCR extends into a region where the concentration of donor-levels is $10^{17} - 10^{14} cm^{-3}$. (3) When we bias the sample from $V_r = 1.5V$ to $V_r = 4V$, the SCR extends into a region where the concentration of donor-levels is $10^{14} cm^{-3}$ (see Fig. 5.11a). According to this description, if we apply the DLTS technique using the bias voltage mentioned in cases (1), (2) and (3), we should obtain the capture cross section and the position of donor-levels for different concentrations.

Fig. 5.12 shows the DLTS diagrams obtained under dark conditions with the bias voltage in cases (1), (2) and (3). These diagrams are represented by the black, the red and the blue line respectively, and they were obtained under the assumption that the operation of the device was modeled by a capacitor connected in series with a resistance. For this reason, C_p transients and G transients were measured by the BOONTON to calculate C_s transients (explained in Section 5.3.1). These C_s transients were analyzed at $t_1 = 20ms$ and $t_2 = 200ms$ to obtain the DLTS diagrams of Fig. 5.12.

Fig. 5.12: DLTS diagram obtained by evaluating C_s at $t_1 = 20\text{ms}$ and $t_2 = 220\text{ms}$ after applying different reverse voltages.

Table 5.I: Features of the electron-traps detected with different bias voltages. The values of ΔH provide the estimated position of the electron-traps with respect to the CB.

Bias	Level 1			Level 2		
V=0/-0.5V	ΔH 0.09eV	σ_n $9.2 \cdot 10^{-23}\text{cm}^2$	N_T $> 1.3 \cdot 10^{14}\text{cm}^{-3}$	---	---	---
V=-0.5/-1V	ΔH 0.08eV	σ_n $2.4 \cdot 10^{-22}\text{cm}^2$	N_T $1.3 \cdot 10^{14}\text{cm}^{-3}$	ΔH 0.21eV	σ_n $2.6 \cdot 10^{-21}\text{cm}^2$	N_T $> 1.8 \cdot 10^{13}\text{cm}^{-3}$
V=-1.5/-4V	---	---	---	ΔH 0.18eV	σ_n $6 \cdot 10^{-21}\text{cm}^2$	N_T $1.8 \cdot 10^{13}\text{cm}^{-3}$

The DLTS diagrams of Fig. 5.12 show positive ΔC_s peaks related to majority carrier traps. Since we assume that every semiconductor layer of the structure of the device is n-type (Fig. 5.10), we can consider that the carrier traps detected in the device are electron-traps. The Arrhenius plot of each electron-trap was obtained by analyzing C_s transients at different temperatures and using different windows rate WR (t_1 and t_2), as described in Section 5.3.1. From the slope and the interception of the each Arrhenius plot we obtained the ΔH and the apparent capture cross section respectively. The concentration of electron-traps (N_T) was determined using equation (5.26) of Section 5.2.2.c, assuming that $t = \infty$ corresponds to the time at which the shape of the C_s transient becomes practically flat. These results are summarized in Table 5..

Depending on the value of ΔH and σ_n , we have classified the electron-traps in two types, “Level 1” and “Level 2”. Electron-traps that correspond to Level 1 are detected when the device is biased from $V_T = 0V$ to $V_T = 0.5V$. Under these conditions the SCR extends into a region with a high concentration of donor-levels associated to Ti atoms, around $10^{19} - 10^{17} \text{cm}^{-3}$ (according to the CV measurements of Fig. 5.11). Therefore, $\Delta H \sim 0.09\text{eV}$ and $\sigma_n \sim 10^{-22} \text{cm}^2$ correspond to electron-traps present in regions with high Ti concentrations. Electron-traps that correspond to Level 2 are detected when the device is bias from $V_T = 1.5V$ to $V_T = 4V$. Under these conditions the SCR extends into a region with a low concentration of donor-levels associated to Ti atoms, around 10^{14}cm^{-3} (according to the CV measurements in Fig. 5.11). Therefore, $\Delta H \sim 0.2\text{eV}$ and $\sigma_n \sim 10^{-21} \text{cm}^2$ correspond to electron-levels present in regions with low Ti concentrations. Both types of electron-traps, Level 1 and Level 2, are detected when the device is biased from $V_T = 0.5V$ to $V_T = 1V$ and the SCR extends into regions where the concentration of donor-levels vary from high concentration (10^{17}cm^{-3}) to low concentration (10^{14}cm^{-3}).

The positions of “Level 2” inside the Si bandgap fits with the position of the energy levels introduced by Ti atoms in [Olea'08]. This feature seems to indicate that Level 2 is related to the presence of Ti atoms. If we consider that electron-traps labeled as “Level 1” and “Level 2” correspond to the presence of Ti atoms, the analysis mentioned above may indicate that the energy levels introduced by Ti atoms reduce its capture cross section and move closer to the CB when the Ti concentration is increased. This hypothesis is in agreement with [Krich'12], where the authors consider that the lifetime recovery reported in [Antolín'09] can be associated to variations in the positioning of the energy levels and not to the formation of an IB. However, it must be emphasized that we cannot conclude that the electron-traps detected in the device are associated to Ti atoms, nor that Level 1 and Level 2 correspond to the same impurity atom or crystalline defect. Indeed, the concentrations of these electron-levels, $\sim 1.3 \cdot 10^{14} \text{cm}^{-3}$ for Level 1 and $1.8 \cdot 10^{13} \text{cm}^{-3}$ for Level 2, do not correspond to either the donor-level concentrations, nor to the Ti concentration.

The parameters of the electron-traps studied in this Section have been obtained analyzing the transient of C_S instead of the transient of C_S^2 . This procedure is valid in this case because the concentration of electron-traps is at least ten times lower than the concentration of N_{SCR} for every case (1), (2) and (3). The inaccuracy introduced in the DLTS diagrams due to analyzing C_S instead of C_S^2 leads to deviations of 0.14% due to the use of the approximation $\sqrt{1 - \frac{N_T}{N_{SCR}}} \approx 1 - \frac{N_T}{2N_{SCR}}$.

5.4.3 Experimental results in IBSCs based on HMAs

In this Section we analyze the IBSCs based on the ZnTe:O HMA studied in Chapter 2. The first results shown in this Section correspond to the IBSC prototype R1030 and its reference solar cell R1024, whose structures are depicted in Fig. 2.2. Note that in the structure of the reference solar cell there is no presence of O.

CV measurements of samples R1030 and R1024 led to similar results. In Fig. 5.13 (left), we show a representative result obtained with the IBSC prototype R1030 under dark conditions. This result was obtained assuming that, for small-signal voltages, the device under study operated as a capacitor connected in parallel with a resistance. The distribution of the charge density of the SCR (Fig. 5.13 right) was obtained assuming a dielectric constant of $\epsilon = 9.8$ [Constable'12] and an area of 4.15 mm^2 , equal to the area of the p-n junction.

Fig. 5.13: (left) CV measurement at 300 K under the assumption that the device operates as a capacitor connected in parallel with a resistance. (right) Distribution of the charge density of the SCR. In this figure the doping level of the n-emitter and the p-emitter are plotted for comparison.

According to Fig. 5.13 (right), the SCR extends along $\sim 1 \mu\text{m}$. This extension is wider than the thickness of ZnTe:O layer (Fig. 2.2), which seems to indicate that the SCR extends from the n-emitter to the p-emitter. In addition the value of N_{SCR} ($2 \cdot 10^{18} \text{ cm}^{-3}$) is closer to the expected doping level for the n-emitter ($5 \cdot 10^{18} \text{ cm}^{-3}$) than the expected doping level for the ZnTe:O layer (10^{16} cm^{-3} [Wang'10]). Under these circumstances, the information provided by the DLTS technique (Fig. 5.14) should correspond to the n-emitter of samples R1030 and R1024 and not to the ZnTe:O layer.

Fig. 5.14: (a) DLTS diagram obtained by evaluating C_p in $t_1 = 40\text{ms}$ and $t_2 = 400\text{ms}$ after applying a reverse voltage $V_r = 4\text{V}$. In this diagram the positive peaks evidence the presence of majority carrier traps. (b) Arrhenius plot of the carrier traps detected with the DLTS technique. ΔH and the apparent capture cross section are obtained from the slope and the intersection of the linear fits respectively.

Fig. 5.14 (a) shows the DLTS diagrams that correspond to samples R1030 and R1024. In this figure, positive ΔC_p peaks are related to majority carrier traps. The features

of these traps, ΔH and capture cross section, are obtained from the slope and the intersection of the Arrhenius plots depicted in Fig. 5.14 (b), and the concentration (N_T) by applying the equation (5.26). Similar results are obtained from one sample to another, which supports the idea that, in samples R1030 and R1024, the DLTS technique provides information of traps located in the same semiconductor layer, which should be the n-emitter layer. According to this, the majority carrier traps are electron traps, placed at ~ 0.7 eV below the CB.

In sample R1030, the energy levels located inside the ZnTe:O bandgap cannot be studied with the DLTS technique since the ZnTe:O layer is too narrow. For this reason we need to study another device, the IBSC prototype R770, with a structure similar to that of R1030 (Fig. 2.2) except for every semiconductor layer is twice as thick. In particular, in the sample R770 the thickness of the layer ZnTe:O is $1\mu\text{m}$.

The CV measurement of sample R770 was obtained using the same procedure as that used for the sample R1030. This CV measurement and the corresponding N_{SCR} distribution are plotted in Fig. 5.15.

Fig. 5.15: (left) CV measurement at 300 K under the assumption that the device operates as a capacitor connected in parallel with a resistance. (right) Distribution of the charge density of the SCR.

The N_{SCR} obtained with the R770 sample ($\sim 1 \cdot 10^{17} \text{cm}^{-3}$) is around twenty times lower than the N_{SCR} obtained with the R1030 sample ($\sim 2 \cdot 10^{18} \text{cm}^{-3}$). This indicates that, in the sample R770, the SCR falls in a less doped region. This region must be the ZnTe:O layer, according to the values obtained for x_{SCR} . This means that the ZnTe:O layer has a N_{SCR} higher than that obtained in ZnTe:O materials grown under similar conditions

(10^{16}cm^{-3}) [Wang'10]. As happened in Section 5.4.1, an incredibly large V_{bi} (above 55 V) is obtained from the analysis of the CV measurement of this sample. This large V_{bi} is related to the insignificant variation of x_{SCR} for different V_r , from $1.093\text{ }\mu\text{m}$ to $1.103\text{ }\mu\text{m}$. A possible origin for this large V_{bi} will be explain in Section 5.4.5.

Fig. 5.16: (a) DLTS diagram of the sample R770 and (b) Arrhenius plot corresponding to the minority carrier trap detected.

Fig. 5.16 shows the DLTS diagram and the Arrhenius plot obtained with sample R770. The DLTS diagram was carried out under dark conditions, using voltage pulses that bias the sample at reverse voltages: at $V_r = 0.5V$ during 1 s (aimed to force a net capture of carriers by traps) and at $V_r = 2V$ during 4 s (aimed to force a net emission of carriers from traps). The operation of the device was modeled by a capacitor connected in parallel with a resistance, so C_p transients were measured by the BOONTON. The DLTS diagram of Fig. 5.16 (a) was obtained from the analysis of the transient produced when the solar cell became biased at $V_r = 2V$ ($t = 0$), for $t_1 = 0.3s$ and $t_2 = 3s$.

The DLTS diagram of Fig. 5.16 (a) shows a negative ΔC_p peak related to minority carrier traps. As in Section 5.3.1, the detection of minority carrier traps was unexpected due to the negligible concentration of minority carriers under reverse voltages. Maybe the source of these minority carriers is the free-carrier tails that extend into the depletion region of abrupt p-n junctions [Meijer'83]. Since the ZnTe:O layer is a p-type semiconductor, these minority carrier traps are electron-traps. From the Arrhenius plot of Fig. 5.16 (b) we obtain for these traps values of $\Delta H = 0.38eV$ and $\sigma_n = 2 \cdot 10^{-19}cm^2$. The concentration of electron-traps, $N_T = 1.2 \cdot 10^{14}cm^{-3}$, is obtained from equation (5.26), assuming that $t = \infty$ corresponds to the time in which the C_p transient becomes flat. These traps may correspond to the energy levels introduced by O_{Te} atoms, since they are also located at around 0.4 eV below the CB [Dietz'62;Hopfield'66]. If this is the case, the low concentration of these electron-traps ($N_T = 1.2 \cdot 10^{14}cm^{-3}$) reinforces the results obtained in Chapter 2, where it was suggested that an IB was not formed in the ZnTe:O materials studied in this Thesis because of an insufficient concentration of O_{Te} . However, it must be emphasized that the value of N_T can be underestimated if the concentration of free electrons is lower than the concentration of the electron-traps. This may be the case if the carrier captured comes from free-carrier tails that extend into the depletion region. Finally, it is important to point out that the electron traps detected inside the ZnTe:O bandgap show a low capture cross section, $\sigma_n = 2 \cdot 10^{-19}cm^2$, typical of repulsive centers [Blood'92c]. This feature is positive for IB implementations, since the lower σ_n is, the more likely it is that generation processes compensate recombination processes.

5.4.4 Experimental results in IBSCs based on QDs

In this Section we want to analyze the confined states in the InAs/AlGaAs QDs studied in Chapter 4. The DLTS technique can provide information about these confined states if the SCR of the devices under study falls inside the region with QDs. Unfortunately in the samples studied in Section 4.3, based on InAs/ $Al_{0.3}Ga_{0.7}As$ QDs, the SCR extends from the p-emitter to the n-emitter. The SCR does not fall inside the region with InAs/ $Al_{0.2}Ga_{0.8}As$ QDs of the samples studied in Section 4.2, due to the presence of a 400

nm n-type "field damping layer" (FDL) that sustains most of the depletion region. For this reason, in this Section, we study other QD-IBSC prototypes.

The new devices studied in this Section have the same structure as the one depicted in Fig. 4.1(a), except for the thickness of the FDL which is reduced to 100nm. The doping and thickness of this FDL were designed to sustain only part of the depletion region, so that a portion of the QDs are located inside the SCR. In these samples, the location of QDs inside the SCR was tested using a variant of the photo-capacitance technique [Henry'73]. This technique consists of monitoring the carrier traps located at the SCR of devices by means of optical excitations. In order to avoid that thermal emission processes obscuring the effects of optical transitions, we cooled the samples to 20 K. Under these conditions we measured the small-signal capacitance for $V_r = 0V$ and different monochromatic illuminations. This monochromatic illumination came from the output of a 1/4 monochromator, where the light of an IR lamp was diffracted. The monochromatic beam was mechanically chopped at low frequency (23 Hz), and the alternate voltage signal at the output of the BOONTON (proportional to the capacitance signal) was measured with a lock-in amplifier. The results are plotted in Fig. 5.17.

Fig. 5.17: Photo-capacitance spectrum of carrier traps located inside the SCR of the QD-IBSC with a 400 nm FDL (black curve) and the QD-IBSC with a 100 nm FDL (red curve).

Fig. 5.17 shows that photon energies between 0.25 eV and 0.5 eV produce variations in the capacitance of the QD-IBSC prototype with a 100 nm FDL. This capacitance variation is related to a variation of N_{SCR} , which suggest that optical transitions from 0.25 eV to 0.5 eV modify the charge state of carrier traps located inside

the SCR of this sample. In Section 4.2 we detected IB-CB transitions for the same photon energies. In view of this, it seems logical to associate the carrier traps detected inside the SCR of the QD-IBSC prototype (100nm FDL) with the confined states in InAs/Al_{0.2}Ga_{0.8}As QDs. These traps were not detected in the QD-IBSC prototype with a 400 nm FDL (black curve in Fig. 5.17), which confirms that in this sample the InAs/Al_{0.2}Ga_{0.8}As QDs are not inside the SCR. The results of Fig. 5.17 are relevant because they prove, for the first time, the detection of IB→CB optical transitions by means of capacitive techniques.

DLTS measurements were carried out to determine the capture cross section of the confined states in InAs/Al_{0.2}Ga_{0.8}As QDs. The DLTS diagrams are plotted in Fig. 5.18, where we represent not only the results obtained with the QD-IBSC prototype with a 100 nm FDL, but also the results obtained with the QD-IBSC prototype with a 400 nm FDL and with a reference solar cell. This comparison facilitates the identification of the confined states in InAs/Al_{0.2}Ga_{0.8}As QDs with respect to other energy levels resulting from crystalline defects. The DLTS diagrams of Fig. 5.18 were obtained under dark conditions, using voltage pulses that bias the samples at: at $V_f = 0V$ during 0.5 s (to force a net capture of carriers by traps) and at $V_f = 2V$ during 99.5 s (to force a net emission of carriers from traps). The operation of the devices was modeled by a capacitor connected in parallel with a resistance. The C_p transients measured with the BOONTON was analyzed for $t_1 = 9.7s$ and $t_2 = 97s$.

Fig. 5.18: DLTS diagrams that correspond to a reference solar cell (black curve), a QD-IBSC prototype with QDs located outside of the SCR (blue curve) and a QD-IBSC prototype with QDs located inside the SCR (red curve). In these diagrams the positive peaks evidence the presence of majority carrier traps and negative peaks

evidence the presence of minority carrier traps.

The DLTS diagrams of Fig. 5.18 show peaks centered at similar temperatures, positive peaks centered at around 300 K (related with majority carrier traps) and negative peaks centered at 260 K and 192 K (related with minority carrier traps). Since these peaks appear in the reference solar cell, they cannot be associated to the confined states in InAs/Al_{0.2}Ga_{0.8}As QDs. These peaks must be associated to energy levels that emerge inside the bandgap as a result of crystalline defects in Al_{0.2}Ga_{0.8}As. In the DLTS diagram of the QD-IBSC with a 400 nm FDL, a negative ΔC_p is obtained at temperatures below 140 K. This ΔC_p should correspond to neither of the confined states, since in this sample the InAs/Al_{0.2}Ga_{0.8}As QDs should be out of the SCR. However this negative ΔC_p does not appear in the reference solar cell, and therefore it may be related to crystalline defects that emerge because of the strain accumulated during the QD growth. Therefore, the only peak that can be related to the confined states in InAs/Al_{0.2}Ga_{0.8}As QDs is the peak centered at 153 K, since it only appears in the QD-IBSC prototype with QDs located inside the SCR. This negative peak is related to minority carrier traps, which in this case are hole-traps since in these samples the SCR falls in a n-type region (Fig. 4.1). However, the features of hole-traps disagree with the features of the confined states that define the IB in InAs/Al_{0.2}Ga_{0.8}As QDs. While hole-traps should be closer to the VB, the confined states that form the IB are close to the CB.

To test whether the hole-traps detected in the QD-IBSC prototype with QDs inside the SCR (associated with the peak centered at around 153 K in Fig. 5.18) correspond to IB-states, we carried out DLTS measurements under illumination conditions. We used a broadband infrared (IR) source to illuminate the samples with photon energies lower than 0.7 eV (produced by a blackbody IR emitter filtered with a GaSb wafer). In Section 4.2, the same illumination produced optical excitations involving the confined states in InAs/Al_{0.2}Ga_{0.8}As QDs. For this reason, if the hole-traps corresponded to confined states, we would expect the presence of optical excitations to reduce the concentration of holes emitted thermally and, therefore, to reduce the peak obtained at 153 K in the DLTS diagram.

Fig. 5.19: DLTS diagrams obtained under dark conditions (solid lines and circles) and under the illumination of photon energies below 0.7 eV (dashed lines and stars). Black curves correspond to the reference solar cell, blue curves correspond to the QD-IBSC prototype with QDs located out of the SCR and red curves correspond to the QD-IBSC prototype with QDs located inside the SCR.

Fig. 5.19 compares the DLTS diagrams obtained under dark conditions with the DLTS diagrams obtained under illumination. This figure reveals that optical excitations do not modify the concentration of carriers emitted from the hole-traps associated to the peak centered at 153 K. This fact suggest that these traps are not the confined states in InAs/Al_{0.2}Ga_{0.8}As QDs. On the other hand, the results depicted in Fig. 5.19 reveal that the presence of optical excitations modifies the concentration of carriers emitted from hole-traps associated to crystalline defects in the reference solar cell. This is in agreement with the results obtained in Section 4.3, where optically active defects were detected in the reference solar cell. The presence of these defects led to an extended spectral response down to 1.1 eV. This absorption threshold is in agreement with the location of the hole-traps detected in the reference solar cell, at around 0.79 eV above the VB according to the Arrhenius plot of Fig. 5.20.

Fig. 5.20: Arrhenius plot corresponding to the optically active hole- traps detected in the reference solar cell.

In summary, we have not been able to identify carrier traps associated with the confined states in $\text{InAs}/\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ QDs with the DLTS technique. However, according to the simulations of Fig. 5.21, carrier traps with features similar to the features of confined states ($\Delta H = 0.35 \text{ eV}$ and σ_n in the $10^{-12} - 10^{-20} \text{ cm}^{-2}$ range) should be detectable in the DLTS diagrams shown in this Section. Besides, the photo-capacitance spectrums shown in Fig. 5.17 confirm the presence of confined states inside the SCR on the sample with 100nm FDL, at 0.35 eV below the CB. Maybe the reason for not detecting these states with the DLTS technique is that the presence of crystalline defects obscures their detection. We hope that future works will be able to make advances in this sense.

Fig. 5.21: Simulation of the DLTS diagrams corresponding to two types of electron-traps. The position of these traps inside the bandgap is similar to the position expected for confined states in InAs/Al_{0.2}Ga_{0.8}As QDs. These diagrams are obtained using the equations of Section 5.2.2.c.

5.4.5 Origin of large built-in voltages obtained from CV measurements

As mentioned in Sections 5.4.1 and 5.4.3, the analysis of the CV measurements of some p-n junctions led to incredibly large V_{bi} , several orders of magnitude above expected values. In this Section we propose a possible explanation for this phenomenon. This explanation is based on the fact that the presence of free-carrier tails inside the depletion region modifies the N_{SCR} and the electric field of the SCR, as illustrated in Fig. 5.22. In this figure, we represent the N_{SCR} as ρ/e and the electric field of three different devices: a Schottky diode based on p-type GaAs ($N_A = 1 \cdot 10^{15} \text{ cm}^{-3}$), a p-n junction with a strongly doped n-layer ($N_D = 1 \cdot 10^{17} \text{ cm}^{-3}$ and $N_A = 1 \cdot 10^{15} \text{ cm}^{-3}$) and a p-n junction with an even more strongly doped n-layer ($N_D = 3 \cdot 10^{18} \text{ cm}^{-3}$ and $N_A = 1 \cdot 10^{15} \text{ cm}^{-3}$). These data were simulated using PC1D.

Fig. 5.22: The ρ/e (a) and the electric field (b) of three different devices: a Schottky diode based on p-type GaAs ($1 \cdot 10^{15} \text{ cm}^{-3}$), a p-n junction with a strongly doped n-layer ($N_D = 1 \cdot 10^{17} \text{ cm}^{-3}$ and $N_A = 1 \cdot 10^{15} \text{ cm}^{-3}$) and a p-n junction with an even more strongly doped n-layer ($N_D = 3 \cdot 10^{18} \text{ cm}^{-3}$ and $N_A = 1 \cdot 10^{15} \text{ cm}^{-3}$). The position $x = 0 \mu\text{m}$ corresponds to the metal-semiconductor junction and the p-n junction. These curves are simulated using PC1D.

Fig. 5.22(a) shows the N_{SCR} of the three devices. In the case of the Schottky diode (black curve) this charge density is negative and is related to N_A^- . In the case of the p-n junctions (blue and red curves) this charge density is also negative and its value is increased with respect to N_A^- in the first 100 nm due to the diffusion of electrons from the n-layers. The presence of these electron tails modifies the electric field, especially at $x = 0\mu\text{m}$, as illustrated in Fig. 5.22 (b). Using PC1D we can obtain for each device the corresponding $\mathcal{E}_0$ for different V_r . From these data, applying the Gauss' theorem and the procedure explained in Section 5.2.1.a, we can simulate the CV curves of the devices. These curves are plotted in Fig. 5.23.

Fig. 5.23 Simulated CV curves corresponding to the Schottky diode (black dots), a p-n⁺ junction (blue dots) and a p-n⁺⁺ junction (red dots).

The N_{SCR} and the V_{bi} of each device are obtained from the slope and the intersection of the linear fits of Fig. 5.23. These linear fits present very similar slopes but very different interceptions. This explains why the three devices show a similar N_{SCR} , which agrees with N_A , and very different V_{bi} . The obtained V_{bi} becomes higher than the real built-in voltage, which is around 1.25 eV, as the electron tails increase their concentration, reaching values as high as 30 V in the case of the p-n⁺⁺ junction (red dots Fig. 5.23). In Sections 5.4.1 and 5.4.3 we obtained similar results to the one obtained for the p-n⁺⁺ junction. For this reason we think that the large V_{bi} obtained from CV measurements may be a consequence of free-carrier tails that extend into the depletion region of the p-n junctions.

5.5 Summary

In Chapter 5 we have analyzed the application of CV measurements and DLTS measurements to IBSCs. We have extended the theory behind these techniques to the case of IB-states in Section 5.2. This analysis has revealed that the CV measurements of IB materials can provide values of N_{SCR} modulated by the number of IB-states, depending on whether they are donor and/or acceptor levels. The analysis of Section 5.2 has also revealed that the theory behind the DLTS technique is valid for IB-states and not only for conventional carrier traps. This is because IB-carriers with low mobility are to be expected in IB with narrow bandwidth, especially in IB materials fabricated with QDs, where the mobility of IB-carriers should be zero. As a consequence, DLTS measurements can provide the relative position of the IB within the bandgap of the host semiconductor and the capture cross section of IB-states. To this end it may be necessary to use DLTS diagrams that represent $\Delta(C^2)$ instead of ΔC . This depends on the electron-occupancy of the IB-states placed in the neutral regions. This electron-occupancy, which is determined by the acceptor or donor nature of the IB-states and the doping level of the IB material, is measurable with the DLTS technique.

In Section 5.3 we have detailed the implementation of a DLTS set-up. This experimental set-up resembles a conventional DLTS system with the additional characteristics that are required to characterize IBSCs, including the possibility of measuring $\Delta(C^2)$ instead of ΔC . The implemented set-up can provide, with reasonable accuracy, the DLTS measurements of devices that, for small-signal voltages, operate as capacitors connected in parallel with resistances or capacitor connected in series with resistances. The validity of the results has been tested by reproducing the results obtained with other DLTS systems and fulfilling the requirements of an ISO-9001:2008.

The experimental results obtained with the capacitive techniques used in this Chapter are detailed in Section 5.4. These results correspond to conventional solar cells (Section 5.4.1), Schottky contacts on IB materials based on DLs (Section 5.4.2), IBSCs based on HMAs (Section 5.4.3) and IBSCs based on QDs (Section 5.4.3).

- (1) The conventional solar cells studied in this Chapter 5 are the reference solar cells of Section 3.3. The analysis of these samples is useful to determine the features of the energy states that emerge inside the bandgap of the GaAs grown at low temperature. From the analysis of CV measurements we can see that the GaAs grown at low temperature shows a N_{SCR} of $5 \cdot 10^{17} \text{ cm}^{-3}$. This charge density may correspond to an excessive density of donor-levels introduced by As anti-sites. This kind of energy levels has been detected by means of DLTS measurements. Their position is estimated to be close to the mid-gap of the GaAs, which is in agreement with the results obtained in Section 3.3.1. The sub-bandgap

photocurrent detected in that Section, at photon energies above 0.7 eV, may correspond to these energy levels. This is supported by the results reported in [Brozel'96], where double donor-levels associated to As anti-sites reduce the GaAs absorption threshold at 0.8 eV.

- (2) In Section 5.4.2, we have studied Schottky diodes based on Si:Ti. CV measurements have provided $N_{SCR}(x)$ similar to the Ti depth profile of the c-Si implanted layer. These results seem to indicate that high concentrations of implanted Ti introduce high concentrations of donor-levels inside the Si bandgap. Energy levels inside the Si-bandgap have been also detected with DLTS measurements. These levels are electron-traps with features that vary with the Ti concentration. In particular, we have obtained electron-traps located around 0.09 eV below the CB, with $\sigma_n \sim 10^{-22} \text{cm}^2$, in regions with high Ti concentrations, and electron-traps located around 0.2 eV below the CB, with $\sigma_n \sim 10^{-21} \text{cm}^2$, in regions with low Ti concentrations. The electron-traps located at 0.2 eV below the CB may correspond to energy levels introduced by Ti atoms, according to [Olea'08]. However, we do not know whether the electron-traps located at 0.09 eV below the CB may also be associated to the presence of Ti atoms. If these two types of electron-traps corresponded to Ti atoms, and even more so, if they were the same electron-traps, our results would confirm the hypothesis reported in [Krich'12]. That work supports that a lifetime recovery can be achieved by increasing the Ti concentration, as a consequence of moving the energy levels close to the CB. However, we do not have enough information to confirm this hypothesis, so we should not discard that the lifetime recovery reported in [Antolín'09] is a consequence of the formation of an IB.
- (3) IBSCs based on HMAs have been also studied with capacitive techniques. In particular, we have measured the IBSCs based on the ZnTe:O of the Chapter 2. The DLTS measurements have revealed the presence of electron-traps located at 0.38 eV below the CB of the ZnTe. These traps may correspond to the energy levels introduced by O_{Te} atoms, since they are also located around 0.4 eV below the CB [Dietz'62; Hopfield'66]. If this is the case, it means that the capture cross section measured with the DLTS technique corresponds to the energy levels that form the IB in ZnTe:O. This capture cross section has a low value, of $2 \cdot 10^{-19} \text{cm}^2$, typical of repulsive centers [Blood'92c]. This feature is positive for IB implementations, since the lower σ_n is, the more likely it is that generation processes compensate recombination processes.
- (4) In Section 5.4.4, we have used the DLTS technique to analyze the confined states in the InAs/ $Al_{0.2}Ga_{0.8}As$ QDs corresponding to Section 4.2. However, we have not been able to distinguish the confined states between other carrier traps present in the $Al_{0.2}Ga_{0.8}As$ bandgap. This may be because the presence of carrier traps in this

material obscures the detection of confined states. Some of these carrier traps have been demonstrated to be optically active, in particular traps located at 0.79 eV above the VB. These results are in agreement with the results obtained in Section 4.3, where the reference solar cell showed an extended spectral response down to 1.1 eV. The confined states in the InAs/Al_{0.2}Ga_{0.8}As QDs have been detected using another capacitive technique consisting of measuring the photo-capacitance spectrum of IBSCs. These measurements have proved, for the first time, the detection of IB→CB optical transitions by means of capacitive techniques.

Finally, in Section 5.5, we have researched why the CV measurements of some devices provide built-in voltages two orders of magnitude higher than those expected. We have proposed that the origin of a high V_{bi} may be the presence of free-carrier tails that extend into the depletion region of the p-n junctions. This hypothesis has been validated by PC1D simulations.

6 CONCLUSIONS AND FUTURE WORKS

6.1 Conclusions related to solar cell operation

- The use of low bandgap substrates can degrade the solar cell performance due to the introduction of ohmic losses and the reduction of the fill factor [Marti'13]. This happens if finite mobility carriers are generated in the substrate and extracted with an eV above the substrate bandgap. The reason for this is that under these conditions, the quasi Fermi level of minority carriers become curved at the solar cell/substrate interface (Section 2.4.2).
- In abrupt p-n junctions, the built-in voltage extracted from CV measurements can be incredibly large, reaching several orders of magnitude above expected values. This could be due to modifications of the charge density and the electric field at the space charge region, due to the presence of free-carrier tails inside this region (Section 5.4.5).

6.2 Conclusions related to IBSCs

- In IBSCs with non-optimum bandgaps distribution, non-selective absorption coefficients can lead to higher limiting efficiencies than those provided by selective absorption coefficients [López'14]. This happens in IBs located at deeper positions inside the bandgap when compared to the optimum position. The reason is that, for non-optimum bandgap distributions, non selective absorption coefficients can

provide a better current matching between VB→IB and IB→CB sub-bandgap transitions (Section 3.2).

- The charge density associated to an IB depends on the number of acceptor-states and donor-states that form the IB and the occupation of these states. The features of IBSCs determine the electron-occupancy for the IB-states along the structure of the devices, and therefore the charge density associated to the IB. This charge density can impact on the result of CV measurements, so that the depletion region of IBSCs may be characterized by a charge density (N_{SCR}) that does not necessary have to approximate N_D . This must be taken into account when CV measurements of IB materials are interpreted (Section 5.2.1.a).
- The DLTS technique can be used to obtain the positioning and the capture cross section of the IB-states if IB-carriers have low mobility. This condition is specially fulfilled by IB materials based on QDs since, in this case, IB-carriers are confined inside the nano-structure. The DLTS diagrams corresponding to IBs may require the representation of $\Delta(C^2)$ instead of ΔC . The former happens when the concentration of carriers emitted from the IB is in the same order of magnitude as in the doping level. Under these circumstances it may not be possible to determine the concentration of IB-states with the DLTS technique (Section 5.2.2.d).

6.3 Conclusions related to IBSC implementations

- In ZnTe:O solar cells manufactured at the Universidad of Michigan we have identified the three optical transitions, VB→IB, IB→CB and VB→CB (Section 2.4.1). In particular, the IB→CB transitions have shown a strong selective character which suggests that in these solar cells the energy levels that form the IB are localized states. An insufficient concentration of O_{Te} may be the reason for the later. In spite of this, the energy levels that form the “IB” have low capture cross section ($\sigma_n = 2 \cdot 10^{-19} \text{cm}^2$) which is positive for IB implementations, since the lower σ_n is, the more likely it is that generation processes compensate recombination processes.
- IBSC prototypes based on Si:Ti (fabricated by means of ionic implantation and pulsed laser melting annealing in collaboration with the Universidad Complutense de Madrid and the Universidad Politcnica de Catalua) produce photocurrent when they are illuminated by sub-bandgap photon energies (0.75-1 eV). This sub-bandgap photocurrent is generated in the Ti implanted region, which acts as IB material. The Si:Ti IBSC prototypes have a HIT structure, the features of which seem to promote a tunneling-emission from the IB to the CB and obscure the

effects of possible IB→CB optical transitions. As a consequence, a reduction of the effective bandgap of the solar cells impedes a demonstration of the principle of voltage preservation (Section 3.2.1) [Silvestre'13].

- In the above Si:Ti IBSC prototypes, the photon absorption threshold obtained from EQE measurements indicates that the IB is located around 0.35 eV below the CB (Section 3.2.1). However, DLTS measurements indicate that energy levels introduced by Ti atoms may be located at 0.2 eV below the CB in regions with low Ti concentrations (10^{14}cm^{-3}) and at 0.09 eV in regions with high Ti concentrations ($10^{19} - 10^{17}\text{cm}^{-3}$). This variation in the positioning of the energy levels may be the reason for the decrease in their capture cross section when the Ti concentration increases (Section 5.4.2). The reduction of the capture cross section can be considered as a reduction of the non-radiative recombination (NRR). However this phenomenon is not the same as the NRR inhibition predicted by the theory [Luque'06a], since in this case the NRR reduction is not necessarily related to the delocalization of the wave function of the IB-states when the Ti concentration increases.
- Solar cells based on GaAs and grown with MBE at low temperatures, of around 200-250°C (in collaboration with the company RIBER), generate sub-bandgap photocurrent and provide output voltages that exceed the energy of the absorption threshold divided by the electron charge [García-Linares'13b]. The energy levels responsible for these operation principles arise from crystalline defects that are formed during the growth at low temperature. Experimental results indicate that these levels are located close to the mid-gap of the GaAs and participate in two-photon generation processes. However, these results also indicate that the generation processes introduced by the energy levels are weaker than the additional recombination processes, with capture cross sections as large as $1.2 \cdot 10^{-12}\text{cm}^2$ (Sections 3.3.1 and 5.4.1) which prevents a high efficiency solar cell.
- In IBSC prototypes based on InAs/ $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ QDs, fabricated by MBE at the University of Tokyo, it is possible to spectrally resolve E_L . This has been obtained, for the first time, by illuminating the QD-IBSC prototypes solely with low energy photons, capable of pumping electrons only from the IB to the CB. Under these illumination conditions, the spectral resolution of E_L is possible since in these prototypes the saturation current between the VB and the IB is high enough to allow pumping of electrons from the VB to the IB even at low temperatures (Section 4.2) [Datas'15]. The spectral resolution of E_L is also possible by means of capacitive techniques (Section 5.4.4). This opens the path for using capacitive

techniques to characterize the three optical transitions, $VB \rightarrow IB$, $IB \rightarrow CB$ and $VB \rightarrow CB$, in IBSC prototypes.

- IBSC prototypes based on $\text{InAs}/\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ QDs, fabricated by MBE at the University of Tokyo, produce by means of the absorption of two-photons, for the first time at room temperature. This two-photon photocurrent leads to an absorption threshold that corresponds to E_L , which facilitates the demonstration that eV_{OC} surpasses the absorption threshold at room temperature, even under low irradiance conditions (Section 4.3) [López'16].

6.4 Suggestions for future works

The results shown in this Thesis leave many questions unanswered that should be addressed in future works.

- Experimental results have evidenced the two sub-bandgap transitions, $VB \rightarrow IB$ and $IB \rightarrow CB$, in IBSC prototypes based on $\text{ZnTe}:\text{O}$. However, the presence of these transitions has not led to the spectral resolution of two-photon photocurrent, as in the case of QD-IBSCs. The reason for this may be the low value of the absorption coefficient of $IB \rightarrow CB$ transitions and its strongly selective character. In future works, the use of a high power light bias with 0.3-0.5 eV photons should be considered to spectrally resolve the two-photon photocurrent in $\text{ZnTe}:\text{O}$ IBSC prototypes.
- According to the band-anticrossing model [Walukiewicz'00], the $\text{ZnTe}:\text{O}$ IBSC prototypes studied in this Thesis show a bandgap E_G that corresponds to a low O molar composition. An increase in the O_{Te} concentration should be pursued in future works, not only to extend to absorption of photons by $IB \rightarrow CB$ transitions, but also to obtain an optimum bandgap distribution, through a E_L blue-shift. We consider that in future works, the increase in O_{Te} concentration could also be supported by measuring an increase in the E_G value.
- Prior to this Thesis, the inhibition of the NRR was demonstrated in $\text{Si}:\text{Ti}$ materials by proving that a sufficiently high Ti concentration causes the recovery of the carrier lifetime [Antolin'09]. We think that using DLTS measurements instead of lifetime measurements may demonstrate more clearly the NRR suppression. The reason is because with the DLTS technique it can be determined if the reduction of the NRR is due to the formation of an IB [Luque'06a] or if it is a consequence of the movement of the energy levels towards shallow positions [Krich'12]. This could be

studied in future works by means of measuring and comparing the capture cross section of deep levels with concentrations above and below the Luque limit.

- In this Thesis DLTS measurements have provided the capture cross section of energy levels inside the bandgap of different materials under dark conditions. This capture cross section corresponds to the absorption of thermal photons. The optical cross section corresponding to the absorption of photons coming from “hot” sources can also be obtained by using similar techniques to DLTS [Blood'92f]. These techniques consist of measuring the emission rate of carriers during the optical excitations processes that take place when devices are illuminated with a specific photon flux. In future works, the use of these techniques to obtain the optical cross section can be useful to characterize the absorption processes involving sub-bandgap transitions.
- Energy levels resulting from crystalline defects have also fulfilled the main operation principles of an IB: the generation of two-photon sub-bandgap photocurrent and the production of an output voltage higher than E_L and E_H . However, these energy levels introduce recombination processes that are stronger than the generation processes. It would be interesting to study the potential of these energy levels to implement an IB.
- The IBSC prototypes based on InAs/Al_{0.3}Ga_{0.7}As QDs studied in this Thesis have also shown advances towards the demonstration of operation principles under real operation conditions. In particular, these prototypes have demonstrated the production of two-photon photocurrent and the production of an output voltage that exceeds the absorption threshold at room temperature and under similar illumination conditions, equivalent to 0.5 suns [López'16]. However, in these devices the thermal escape is still strong so that at room temperature eV_{OC} cannot overcome both sub-bandgaps (E_L and E_H). Future works should try to suppress this thermal escape, for example, by increasing E_L by growing larger QDs or using host materials with larger bandgaps. We suggest the fabrication of InAs/AlGaAs prototypes with an Al content higher than 30%. The engineering of these QDs, in terms of composition and size, may lead to an increase of E_L . These improvements may lead the way to the next experimental step. This step consists of demonstrating the operation principles of IBSCs at the maximum power operation point, which means at forward voltage bias close to V_{OC} .
- The IBSC prototypes studied in this Thesis have shown a small spectral response at sub-bandgap photon energies. The IBSC research needs to address this problem, for example, by employing light trapping techniques. In this direction, the use of texturing, reflective back surfaces, plasmonics [Mendes'13] and diffraction

gratings [Mellor'11] should be investigated to increase the absorption of photons with energies below E_G .

Publications related to this Thesis

Publications in International Journals

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