



Fabrication, characterization and simulation of III-V on Si multi-junction solar cells

Elias Veinberg Vidal

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THÈSE

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préparée au sein du **Laboratoire CEA/LETI**
dans l'**École Doctorale EEATS**

Fabrication, caractérisation et simulation de cellules solaires multi-jonction III-V sur silicium

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General Introduction

Photovoltaic solar energy is a possible solution to supply the growing electricity demand, while reducing at the same time climate change due to greenhouse gas emissions. Achieving solar cells with high electrical conversion efficiency and the reduction of their production costs are the main objectives of this PhD work.

Si solar cells with record efficiencies over 26% have been recently demonstrated, approaching the Si single-junction limit of 30%. Multi-junction solar cells based on III-V materials can overcome this limit: efficiencies over 45% have been reported for a 5-junction under 1 sun and for a 4-junction under a concentrated illumination of 300 suns. Due to their elevated cost, these cells could be used in terrestrial applications only if operated under very high sunlight concentration for commercial terrestrial applications, which in turn increases the module and system complexity.

An intermediate solution consists in fabricating high efficiency III-V solar cells on Si substrates, which are less expensive than the III-V or Ge substrates used in conventional multi-junction solar cells. Mechanical-stacked and wafer-bonded solar cells, which avoid the unresolved issues of III-V on Si epitaxy, have already demonstrated efficiencies over 33%. This, combined with the recent advancements in the field of substrate reuse, predict a promising future for III-V on Si tandem solar cells, which could lead the next generation of high-efficiency and low-cost photovoltaics.

In this PhD work, 2-junction AlGaAs//Si and 3-junction GaInP/AlGaAs//Si tandem solar cells were fabricated. The Si bottom subcell and the III-V top subcell(s) were joined together by wafer bonding, resulting in a 2-terminal III-V//Si solar cell configuration.

This dissertation is organized into four chapters. The first chapter introduces the context of the photovoltaic market and the basic principles of solar cell operation. The motivation for III-V on Si solar cells is also presented, together with a literature review of the most remarkable realizations and the different fabrication approaches.

Chapter 2 focuses on wafer bonding. The different wafer bonding techniques reported in the literature are reviewed and the ones performed in this study are discussed in detail,

including an innovative approach showing promising industrialization potential and thus, opening a new path for III-V on Si integration. Finally, the GaAs//Si bonding interface electrical properties are analyzed using dedicated test devices originally conceived at CEA, allowing to evaluate the interface resistance and the conduction mechanism.

Chapter 3 presents the design and fabrication of the III-V and Si subcells. Optimizations in design and cell processing were carried out thanks to simulations and characterization of device performance, leading to satisfactory results, including record efficiencies. PC1D simulations allowed to identify the key factors that limit the Si subcell performance and possible improvement strategies. Si bottom subcells are fabricated using different diffusion or implantation processes for the emitter and back surface field formation. Their impact on cell performance is analyzed experimentally by carrier lifetime and quantum efficiency measurements. Finally, the fabrication process after wafer bonding and anti-reflection coating optimization by transfer-matrix simulation methods are also presented and discussed.

In Chapter 4, a new light current-voltage characterization method, specially adapted for multi-junction solar cells under concentrated light, is developed in order to correctly assess the efficiency of the fabricated III-V on Si tandem cells. First, the challenges and requirements for the accurate MJSC efficiency measurement are reviewed, together with the state-of-the-art of existing characterization methods. Then the measurement principle of the new method is explained, including the manufacturing details of the required pseudo-isotypes. Finally, the validity of the method is demonstrated by measuring 2-junction and 3-junction III-V on Si tandem solar cells, obtaining the electrical conversion efficiency.

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Nomenclature

Acronyms / Abbreviations

1J single-junction solar cell

2J 2-junction solar cell

2T 2-terminal configuration

3J 3-junction solar cell

3T 3-terminal configuration

4J 4-junction solar cell

4T 4-terminal configuration

μ -PCD Microwave detected Photo-Conductance Decay

a-Si Amorphous Silicon

AEY Annual Energy Yield

AFM Atomic Force Microscopy

ALD Atomic Layer Deposition

AlGaAs Aluminum Gallium Arsenide

AlInP Aluminum Indium Phosphide

AM0 reference spectrum outside the atmosphere

AM1.5D direct or normal reference spectrum

AM1.5G hemispherical global reference spectrum

AM Air Mass

APS Active-Pixel Sensors

ARC Anti-Reflection Coating

ASTM American Society for Testing and Materials

ASU Arizona State University

BLII Beam Line Ion Implantation

BSF Back Surface Field

BSRV Back Surface Recombination Velocity

c-Si Crystalline Silicon

CCD Charge-Coupled Device

CdTe Cadmium Telluride

CEA Commissariat à l'Énergie Atomique et aux énergies alternatives

CIGS Copper Indium Gallium Selenide

$CM(\text{sub } i / \text{sub } j)$ Current-Matching ratio between two subcells i and j

CMOS Complementary Metal-Oxide-Semiconductor

CMP Chemical-Mechanical Polishing

CNRS Centre national de la recherche scientifique

CPV Concentrated Photovoltaics

CSEM Centre Suisse d'Électronique et de Microtechnologie

CZ Czochralski

DOPT Département d'Optique et de Photonique

DTSI Département Technologies Silicium

DUT Device Under Test

EDX Energy-Dispersive X-ray spectroscopy

EL(λ)	spectral Electro-Luminescence
ELO	Epitaxial Lift-Off
EPBT	Energy Payback Time
EPFL	École Polytechnique Fédérale de Lausanne
<i>EQE</i>	External Quantum Efficiency
ERE	External Radiative Emission efficiency
erfc	complementary error function
erf	error function
Fraunhofer-ISE	Fraunhofer-Institut für Solare Energiesysteme
FAB	Fast Atom Beam
<i>FF</i>	Fill Factor
FSRV	Front Surface Recombination Velocity
FZ	Float Zone
GaAs	Gallium Arsenide
GaAsP	Gallium Arsenide Phosphide
GaInP	Gallium Indium Phosphide
GaP	Gallium Phosphide
Ge	Germanium
HCl	hydrochloric acid
HCPI	Hybrid Corrected Pseudo-Isotype characterization method
HCPV	High Concentrated Photovoltaics
HF	Hydrofluoric acid
HF	hydrofluoric acid
HIT	Heterojunction with Intrinsic Thin layer

HIT	Heterojunction with Intrinsic Thin-layer
HRTEM	High Resolution Transmission Electron Microscopy
ICP	Inductively Coupled Plasma
IEC	International Electrotechnical Commission
IES–UPM	Instituto de Energía Solar – Universidad Politécnica de Madrid
INES	Institut National de l’Énergie Solaire
InGaAs	Indium Gallium Arsenide
InP	Indium Phosphide
<i>IQE</i>	Internal Quantum Efficiency
IQE	International Quantum Epitaxy, a semiconductor company
IR	infrared
LBIC	Laser Beam Induced Current
LC	Luminescent Coupling
LCOE	Levelized Cost of Energy
LCPV	Low Concentrated Photovoltaics
LETI	Laboratoire d’Électronique et de Technologie de l’Information
LITEN	Laboratoire d’Innovation pour les Technologies des Energies Nouvelles
LPF	Long Pass Filter
LTM	Laboratoire des technologies de la Microélectronique
mc-Si	Multi-Crystalline Silicon
MJSC	Multi-junction Solar Cell
MOVPE	Metalorganic Vapor Phase Epitaxy
NREL	National Renewable Energy Laboratory
OSMSS	One-Sun Multi-Source Simulator

PECVD	Plasma-Enhanced Chemical Vapor Deposition
PERC	Passivated Emitter Rear Cell
PERL	Passivated Emitter with Rear Locally diffused
PIII	Plasma Immersion Ion Implantation
PV	Photovoltaics
QSSPC	Quasi-Steady-State Photo-Conductance
RCA	Radio Corporation of America cleaning sequence
RCAST	Research Center for Advanced Science and Technology
RIE	Reactive-Ion Etching
RMS	Root-Mean-Square
SAB	Surface Activated Bonding
SAM	Scanning Acoustic Microscopy
sc-Si	Single-Crystal Silicon
SC	Standard Cleaning
SEM	Scanning Electron Microscopy
SIMS	Secondary-Ion Mass Spectrometry
Si	Silicon
$SMR^{(\text{sub } i / \text{sub } j)}$	Spectral Matching Ratio between two subcells i and j
SPF	Short Pass Filter
SRC	Standard Reporting Conditions
SR_{DUT}	spectral response of device under test
SRH	Shockley-Read-Hall recombination
$SR_{\text{ref } i}$	spectral response of reference cell i
$SR_{\text{sub } i}$	spectral response of subcell i

SRV Surface Recombination Velocity

T-HIPSS Terrestrial-High Intensity Pulsed Solar Simulator

TCAD Technology Computer Aided Design

TCO Transparent Conductive Oxide

TDD Threading Dislocation Density

TEM Transmission Electron Microscopy

UNSW University of New South Wales

UV ultraviolet

Symbols

* superscript indicating the value at 1-sun

A solar cell area

α absorption coefficient

C Capacitance

χ electron affinity

D diffusivity

Δn excess minority carrier concentration

e^- electrons

E_g bandgap energy

η electrical conversion efficiency

$\vec{E}$ electric field

G total incident irradiance

G^* reference irradiance defined as 1000 W m^{-2}

G_λ spectral irradiance distribution or spectrum

G_λ^* reference spectrum

h^+	holes
I	electrical current
I_0	diode leakage current, dark saturation current
i	index of the subcell: top or bottom for a 2J solar cell
I_L	light or photo-generated current, photocurrent
I_{MPP}	current at the maximum power point
$I_{ref\ i}^*$	current of reference cell i under the reference spectrum
$I_{ref\ i}^{sim}$	current of reference cell i under the solar simulator spectrum
I_{SC}	short-circuit current
$I_{sub\ i}^*$	current of a subcell i under the reference spectrum
$I_{sub\ i}^{sim}$	current of subcell i under the solar simulator spectrum
J	electrical current density
j	index of the subcell: top or bottom for a 2J solar cell
k	Boltzmann's constant
L	diffusion length
M_i	spectral mismatch correction factor between the reference and subcell i
n	ideality factor
N_0	n-type peak doping
P_0	p-type peak doping
P_{max}	maximum electrical power
q	absolute value of the electron charge
$q\Phi_b$	potential barrier height
R	recombination rate or reflectance
R_{int}	interface resistance

R_S	series resistance
R_{SH}	shunt resistance
T	temperature or transmittance
t'	average of the t^* at different concentrations, measurement time during the flash at which the solar simulator spectrum is recorded
t^*	measurement time during the flash at which $SMR(\text{ref } i / \text{ref } j) = 1$
τ	charge carrier lifetime
V	voltage
V_{MPP}	voltage at the maximum power point
V_{OC}	open-circuit voltage
V_T	thermal voltage
X	concentration level
x_d	doping profile depth factor
X_{opt}	optimum concentration level
x_p	doping profile peak position
$X_{\text{ref } i}$	concentration factor of component reference cell i
$X_{\text{sub } i}$	concentration factor of subcell i

Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university.

The work presented in this thesis was carried out by the author, with the following exceptions:

Fabrication

- GaInP/AlGaAs top subcells for the 3-junction configuration were designed and epitaxially grown by Fraunhofer-ISE. The AlGaAs top subcell epitaxy for the 2-junction configuration was done either by IQE or III-V Lab. The first design was done at CEA/LETI by Pablo Garcia-Linares, Cécilia Dupré, Pascal Scheiblin and Yohan Desières. Following optimizations were carried out by Laura Vauche and by the author.
- Si subcell emitter and BSF formation by thermal diffusion processes was done at CEA/LITEN INES by Yannick Veschetti and Thibaut Desrues. Implantation processes were conducted at the LETI and LITEN by Adeline Lanterne, Coralie Lorfeuvre, Marianne Coig and Frederic Milesi.
- Wafer bonding was done in the CEA/LETI DTSE platform. GaAs//Si hydrophilic wafer bonding was carried out by Vincent Larrey and Christophe Lecouvey, while surface activated bonding was conducted by Christophe Morales with engineering expertise from Frank Fournel. Epitaxy of GaAs on Si by MOVPE for the epi-GaAs//GaAs wafer bonding approach was done at LTM-CNRS by Michaël Martin and Thierry Baron. CMP treatment was carried out by Christophe Lecouvey. The entire wafer bonding process integration was done by Laura Vauche, Thierry Salvétat and Céline Brughera.
- Saw-cut in order to manufacture the test devices, presented in section 2.3.2, was conducted by Manon Arch and Daniel Mermin.

- Fabrication process after wafer bonding, including GaAs substrate removal, front metalization, mesa etching, contact layer etching, ARC deposition, back metalization and passivation, was done at the CEA/LETI DOPT platform by Tiphaine Card, Jérémy Da Fonseca, Romain Guiavarch and Vincent Rebeyrol, under the supervision of Christophe Jany.
- Single-layer Si_3N_4 ARC optimization was conducted by Yohan Desières. Double-layer $\text{Si}_3\text{N}_4/\text{SiO}_2$ optimization for the 3-junction and 2-junction structures was carried out by Laura Vauche and by the author respectively.

Characterization

- Surface characterization by AFM was done by Christophe Lecouvey, while deffect mapping using Surfscan and SAM equipment was carried out by Laura Vauche and Céline Brughera. FTIR interface characterization was conducted by Névine Rochat. Ellipsometry GaAs intermediate layer thickness measurements were carried out by Laura Vauche and Christophe Lecouvey. HRTEM and EDX characterization was done at the PNFC platform by Anne-Marie Papon or by SERMA Technologies.
- SIMS measurements of Si subcell emitter doping profiles were conducted by Marc Veillerot. Carrier lifetime measurements using QSSPC were carried out by Thibaut des Desrues, Laura Vauche, Adeline Lanterne and Coralie Lorfeuvre, while μ -PCD measurements were done by Laura Vauche.
- The solar simulator spectrum measurement with a CMOS spectroradiometer was done by Clément Weick at CEA/LITEN INES module characterization platform. *EQE* measurements were conducted by Karim Medjoubi and by the author.

The evaluation of the results was carried out by the author.

Elias Veinberg-Vidal
December 2018

Chapter 1

Introduction: context and basic principles

For more than a century, intensive and large-scale exploitation of petroleum and coal, has significantly disrupted our environment. The combustion of fossil fuels release greenhouse gasses which are the main cause of the current raise in global mean temperature, as shown in figure 1.1 [2], which is known as global warming. In this regard, the Paris agreement was signed in 2015 to respond to the threat of climate change and aims to maintain a rise in global temperature this century below 2 degrees Celsius compared to pre-industrial levels. Yet these sources of energy have allowed the world population to grow enormously and have given us access to a quality of life unequaled in the history of humanity. This trend is likely to continue, as shown by the United Nations prospects predicting a world population growth from 7.6 billion in 2017 to 9.6 billion by 2050 and 11.2 billion by 2100 [3], which together with the increasing standard of living in the developing countries will cause a strong growth in electricity demand [4].

We face then a complex challenge: how to provide energy in a sustainable way to the growing population while maintaining or even increasing the quality of life. These concerns, together with geopolitical tensions in the producing countries and worries about reaching peak oil production, due to the inevitable progressive depletion of deposits, led to strong fluctuations in the prices of fossil fuels, as shown in figure 1.2, with a historical peak in 2008, which is known as the 2000s energy crisis.

Whether to reduce air pollution and global warming, ensure energy independence and safety or to reduce costs and improve efficiency, the world's energy systems have to undergo major changes driven by strong R&D investments in renewable energies. Although now renewables represent only a small part of the total energy system, as shown in figure 1.3,

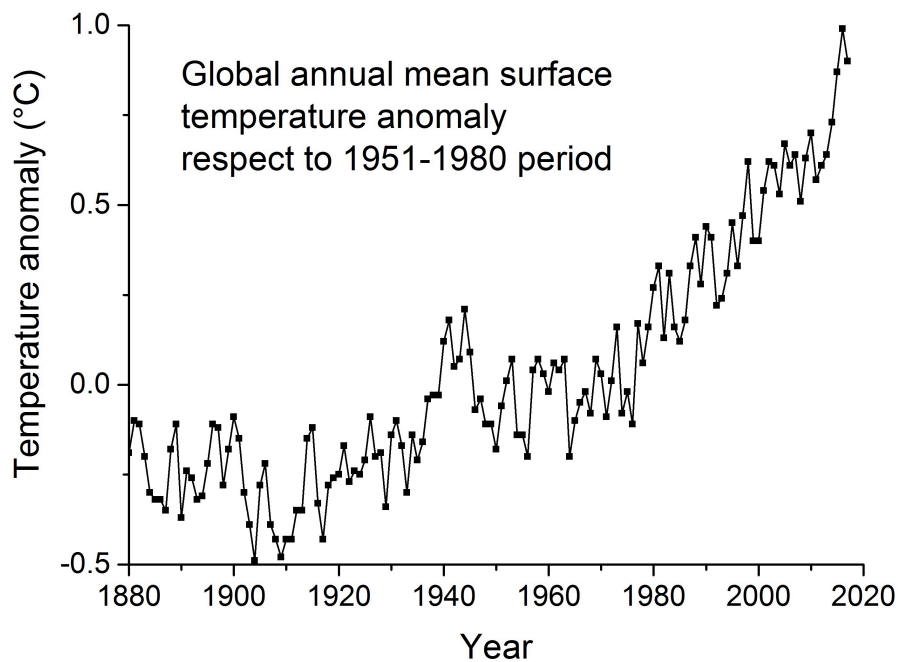


Fig. 1.1 Global annual mean surface temperature anomaly respect to 1951-1980 period. Data from NASA Goddard Institute for Space Studies [2].

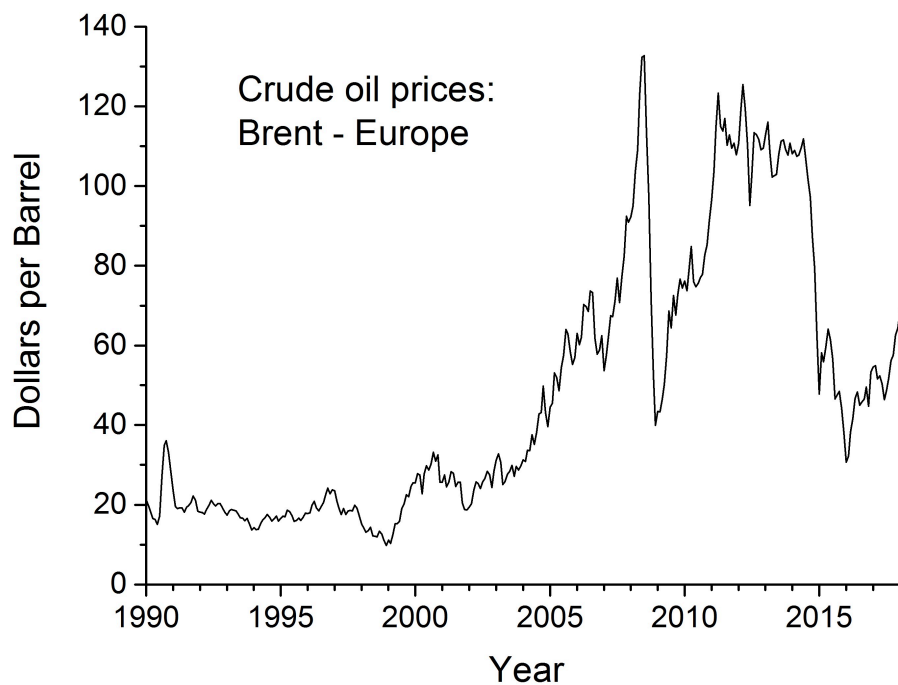


Fig. 1.2 Crude oil prices in dollars per barrel, not seasonally adjusted: Brent - Europe, data retrieved from FRED, Federal Reserve Bank of St. Louis, source: U.S. Energy Information Administration [5].

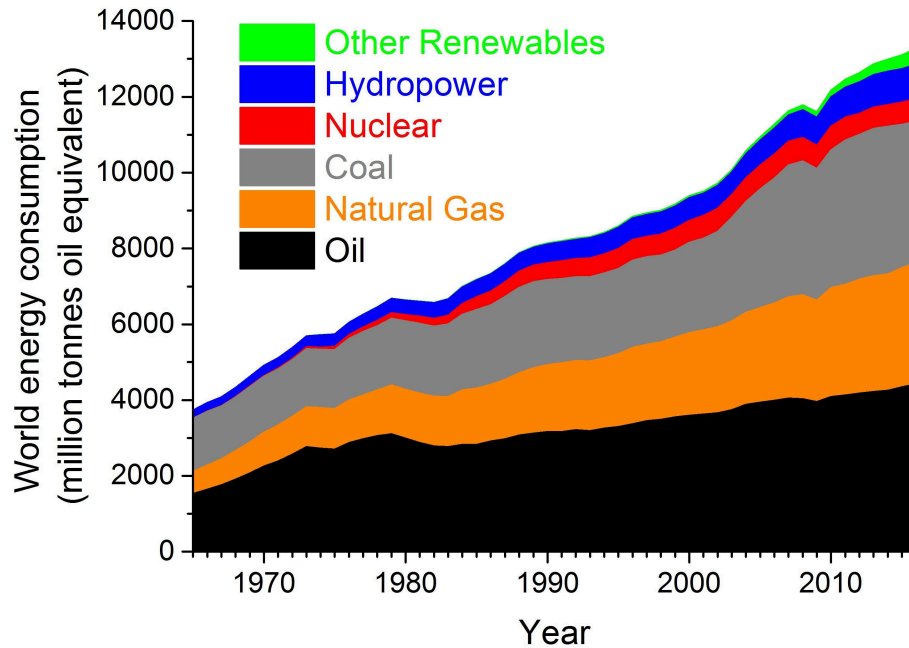


Fig. 1.3 World consumption for different forms of energy in million tonnes oil equivalent, data from [7].

these technologies are evolving rapidly and continue to strengthen their position as viable energy solutions. Over the 2010-2015 period, renewable power generation expanded by more than 30%. In 2016, global renewable electricity generation grew by an estimated 6% and represented around 24% of global power output. Hydropower remained the largest source of renewable power, accounting for around 70%, followed by wind (16%), biomass (9%) and solar (5%) [6].

Solar energy is the original source of almost all forms of energy on earth, including renewable sources like wind (through air heating), hydropower (through the water cycle) and biomass (through photosynthesis), but also fossil fuels, which are essentially stored solar energy through photosynthesis from millions of years ago. The Earth receives annually around 1.5×10^9 TWh of solar energy, while the global consumption in 2016 was about 1.5×10^5 TWh [7], i.e. about 10000 times the energy needs of mankind. Therefore, solar electricity generation has the potential to grow to very large scale. Solar energy is divided in solar thermal, where heat can be used for example to drive a turbine for electricity production, and photovoltaics (PV), a simple and elegant method in which solar cells are used to directly convert sunlight into electricity.

After this short introduction on the global energy context, in the next sections of this chapter the PV market and future outlooks are presented. Then the basic principles of

single and multi-junction solar cell operation are discussed, together with the effect of light concentration. Finally, the motivation for III-V on Si solar cell research and the integration challenges of the different manufacturing approaches are presented, giving an overview of the state-of-the-art for III-V on Si solar cells.

1.1 Context of photovoltaics

PV meets the important requirements of a sustainable energy production because during operation there is no harmful emission, radioactive waste or generation of pollutants, nor any production of noise or other by-products. The energy provided by the Sun is vast, essentially infinite and widely available, making PV a renewable and equitable source of energy, generally applicable to most locations of the earth and specially suitable to isolated locations or even space applications [8].

PV systems have a short energy payback time (EPBT), i.e. the time the system must operate to produce the energy used during its fabrication, of about 1 to 3 years depending on the technology and location [9]. Considering the proven PV high reliability of around 20 to 30 years of useful lifetime, production of new clean energy is guaranteed.

Other advantages of PV are the fast, easy and modular installation together with the low operating costs and maintenance. Nevertheless, solar energy has some disadvantages: sunlight is a diffuse and intermittent energy source due to day night cycle and weather.

French physicist Alexandre-Edmond Becquerel discovered the photovoltaic effect in 1839 [10] and in 1954 the first practical photovoltaic device was demonstrated by Bell Laboratories, with a 6% efficient silicon cell [11]. Nowadays, more than 150 years later, solar PV is a mature technology and, as shown in figure 1.4, in recent years the PV market has become a truly global reality with an exponential deployment rate at international level. In 2017, annual new PV installations reached a new record of 98 GW added to the grid, compared to 76 GW in 2016. The major contributor was China with 53 GW, followed by USA with 10.6 GW. The third position was finally taken over by India that installed 9 GW, ahead of Japan (7 GW) and the European Union (6.5 GW). At the end of 2017, the worldwide PV installed capacity reached 400 GW, after it took the 300 GW mark the year before and the 200 GW level in 2015. By 2021 the global capacity is expected to reach 700 GW [12, 13].

Although a wide variety of PV technologies using different materials exist, PV market is dominated up to 94% by silicon-wafer based solar cells thanks to the maturity and relative low cost production of the silicon industry. The remaining 6% is for thin film technologies made of cadmium telluride (CdTe), copper indium gallium selenide (CIGS) or amorphous

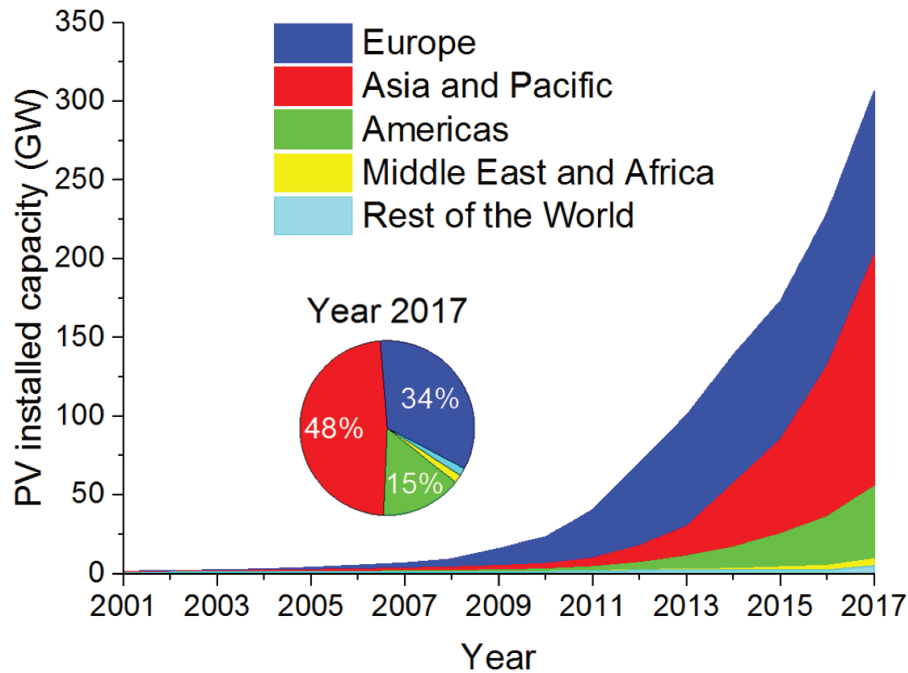


Fig. 1.4 PV cumulative installed capacity by region, data from [14–17]

silicon (a-Si) [9]. Silicon (Si) is indeed one of the most abundant materials in the Earth's crust and is also commonly used in microelectronics. Crystalline silicon (c-Si) solar cells can be divided into single-crystal (sc-Si) and multi-crystalline (mc-Si), accounting for 24% and 70% of total PV production respectively.

The experience or learning curve, shown in figure 1.5, indicates that in the last 36 years the module price decreased by 24% with each doubling of the accumulated module production as a result from economies of scale and technological improvements [9]. Today, utility-scale solar is generally already cheaper, in terms of Levelized Cost of Electricity (LCOE), than new combined cycle gas turbines, coal and nuclear power plants, while rooftop solar is usually cheaper than grid-power [12]. The LCOE is an economic assessment of the average total cost to build and operate a power-generating facility over its lifetime divided by the total energy output over that lifetime and it is used to compare different methods of electricity generation. The cost includes the initial capital, the discount rate and the costs of continuous operation and maintenance.

In conclusion, PV today has demonstrated the maturity of a consolidated industry and is growing very fast worldwide, gaining relevance in significant electricity markets. Growth is expected to continue in the decades ahead and therefore PV technology will become a major source of electricity for the world in the 21st century [19].

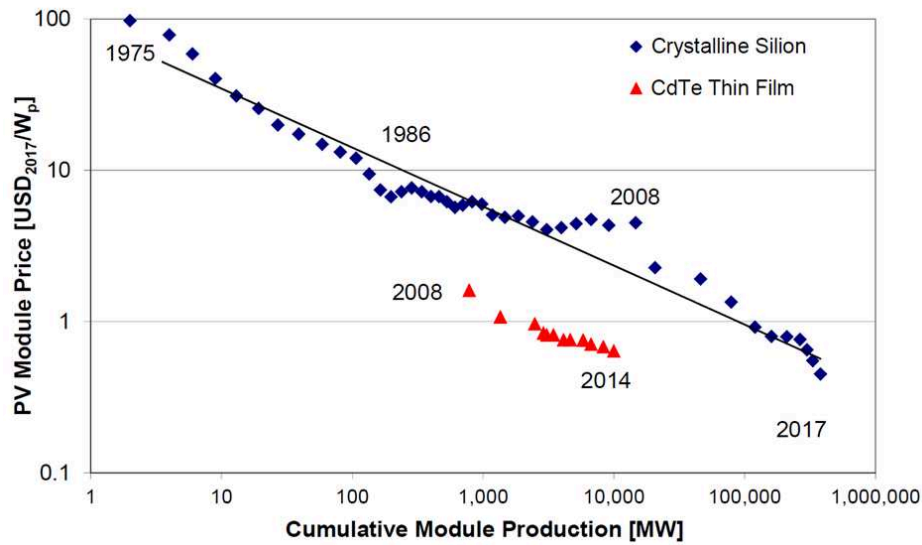


Fig. 1.5 Experience or learning curve for c-Si and CdTe technologies [18].

Challenges on electric grid management due to the intermittence of sunlight (and wind) will have to be addressed. In this regard, the boom of electric vehicles is expected to bolster electricity use and reduce the cost of batteries, which will allow to balance the electric grid by charging them when renewables are generating and wholesale prices are low [20].

1.2 Basic principles of solar cell operation

A solar cell is a device that absorbs sunlight photons to produce free electrons that can be extracted producing an electrical current through an external circuit, converting this way the energy of the Sun into electricity.

1.2.1 Sunlight

The Sun has a surface temperature of about 5700 K [21] and its spectral irradiance or spectrum can be approximated by a blackbody radiator at that temperature following the Planck's radiation law [22]. Therefore, the light emitted by the Sun is composed of many wavelengths, or equivalently photons with different energies, that combined appear white or yellow to the human eye.

The average solar irradiance just outside the Earth's atmosphere, or solar constant, is 1366 W/m^2 [23]. While the solar radiation incident on the top of Earth's atmosphere is relatively constant, the irradiance, G , at the surface of the Earth, varies widely due to day-

night cycle, season of the year, latitude or atmospheric effects like clouds and pollution. The passage through the atmosphere causes a reduction in the power of the solar radiation and a change in the spectral content due to greater absorption or scattering of some wavelengths. These effects depend on the path length through the atmosphere that photons take until reaching the Earth's surface, defined as the air mass (AM), thus when the Sun is just overhead, $AM = 1$.

A total irradiance of 1000 W/m^2 , by tradition called '1-sun' in PV scientific literature, has been defined as the standard reference condition, which corresponds to a distance traveled by the light through the atmosphere 1.5 times greater ($AM = 1.5$) than when the Sun is exactly overhead. Parameters at 1-sun reference conditions will be denoted by an asterisk in the superscript as in $G^* = 1000 \text{ W/m}^2$. The corresponding spectrum can be either the AM1.5G or AM1.5D spectra [24, 25]. The 'G' in AM1.5G stands for global and includes both direct sunlight and diffuse sky radiation produced in the atmosphere through scattering. On the contrary, the AM1.5D spectrum, with 'D' standing for direct, includes only direct or normal radiation and is often used as the reference spectrum when optic systems are used to concentrate the sunlight into a solar cell. Correspondingly, the spectrum outside the atmosphere used for space applications is called AM0 [23]. The AM0, AM1.5G and AM1.5D reference spectra are represented in figure 1.6. As solar radiation passes through the atmosphere, particles and gasses, notably ozone (O_3), carbon dioxide (CO_2), and water vapor (H_2O), absorb the incident photons that have energies close to the bonding energies of these molecules.

1.2.2 Semiconductors and p-n junctions

Solar cells working principle is based on p-n junctions formed by joining n-type and p-type semiconductor materials. Light shining on solar cells produces both a current and a voltage to generate electric power. The incident photons are absorbed by the semiconductor materials that form them, generating free electrons (e^-) that can be collected in the electric contacts of the device. A voltage is then generated and an electric current travels through the external circuit delivering power to the attached load.

Semiconductors are made of atoms bonded together through covalent bonds to form a regular and periodic structure, known as the crystal lattice. Valence electrons from the outer shell are weakly bonded to the nucleus and can be shared with another atoms to form covalent bonds. Electrons forming a covalent bond cannot participate in current flow. However, by thermal excitation or photon absorption, some electrons can gain enough energy to escape from their bound state (valence energy band) and be promoted to a free state (conduction

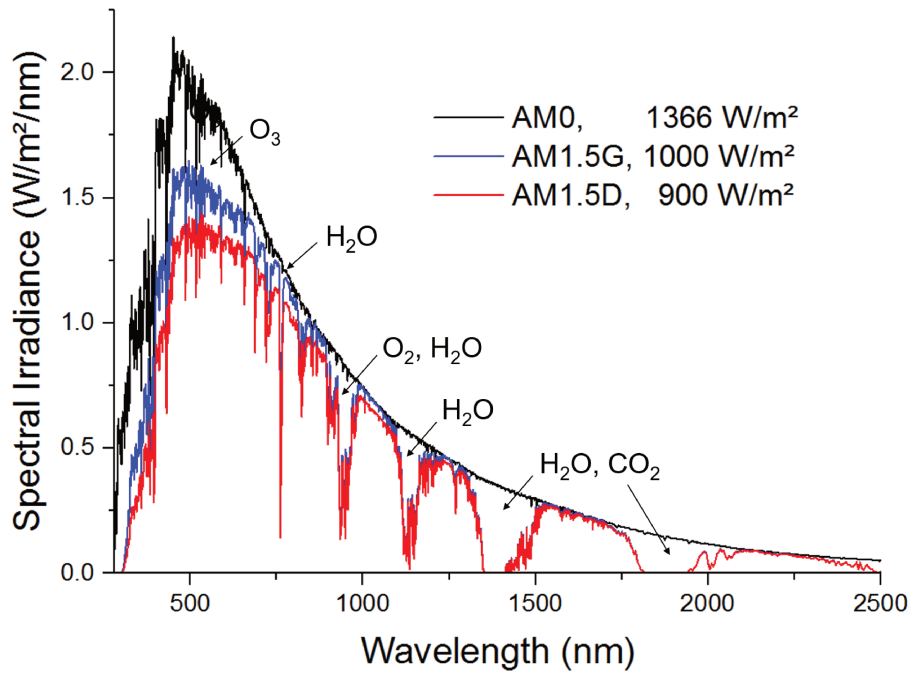


Fig. 1.6 Reference spectrum outside the atmosphere (AM0) [23] compared to the global (AM1.5G) and direct (AM1.5D) reference spectra at the Earth's surface [24]. The main atmospheric gases that absorb solar radiation are also indicated.

energy band). The energy separating the valence and conduction bands is known as the bandgap energy, E_g , and is the minimum amount of energy required for an electron to break free. Therefore, only photons with an energy above the bandgap can be absorbed. The empty space left behind by the excited electrons appears as a positive charge moving through the crystal lattice and is commonly called a hole, h^+ . Conduction in a semiconductor occurs through the movement of free electrons and holes, known as charge carriers. At a temperature close to absolute zero, a semiconductor behaves like an insulator because all the electrons are in their bound state. On the contrary, at room temperature significant number of electrons are free, which enables conduction.

The concentration of electrons or holes in an undoped semiconductor is called the intrinsic carrier concentration and depends on the material bandgap and temperature. The total number of carriers in the conduction or valence band can be increased through doping, which is a technique consisting in adding impurity atoms with more (n-type) or less (p-type) valence electrons than the original material. In n-type semiconductors the majority charge carriers are electrons while the minority charge carriers are holes. Exactly the opposite is true for p-type semiconductors.

As shown in figure 1.7, p-n junctions are formed by joining n-type and p-type semiconductor materials. Since the n-type region has a high electron concentration and the p-type a high hole concentration, carriers diffuse from one side of the junction to the other and recombine, leaving behind the exposed charges of the dopant atoms, which are fixed in the crystal lattice and are unable to move. On the n-type side, positive ion cores are exposed, while negative ion cores are exposed on the p-type side, which creates an electric field, $\vec{E}$. This region is then called the space charge region or depletion region, since the electric field quickly sweeps free carriers out.

Photons of energy below the bandgap cannot be absorbed and thus the material appears transparent to that wavelength. Photons of energy equal to or greater than the bandgap of the material can be absorbed by exciting electrons from the valence band to the conduction band. However, the excess of energy is lost by thermalization as electrons (or holes) quickly relax to the conduction (or valence) band edges, losing the excess energy in the form of heat. Therefore, the bandgap modulates photon absorption and determines the number of photo-generated charge carriers, together with the potential energy that those excited carriers have as compared to their ground state.

With a limited semiconductor thickness, even some photons with energies above the bandgap will not be absorbed. The absorption coefficient, α , determines how far into a material light of a particular wavelength or energy can penetrate before it is absorbed, as described by the Beer-Lambert law:

$$T = 1 - A = e^{-\alpha x} \quad (1.1)$$

where the internal transmittance, T , is the fraction of incident light intensity that is transmitted through a sample of thickness x , taking only into account absorption losses, A . Semiconductors with direct bandgaps have higher absorption coefficients compared to indirect bandgaps and thus require less material thickness to absorb sunlight. Highly energetic photons (short wavelength), such as blue light, have a higher absorption coefficient and thus can be absorbed close to the front surface, while red light (lower energy, longer wavelength) is absorbed less strongly, if the energy is above the bandgap, and thus usually deeper into the material.

When a semiconductor is illuminated, photons are absorbed and free charge carriers are generated. However, the excited electrons tend to lose energy and re-occupy an available low energy state in the valence band in a process called recombination. If the electrons recombine before being collected in the external circuit the potential energy is dissipated in the form of light (an emitted photon) or heat, depending on the recombination mechanism, and thereby no current or power can be generated. The average distance traveled by free carriers before

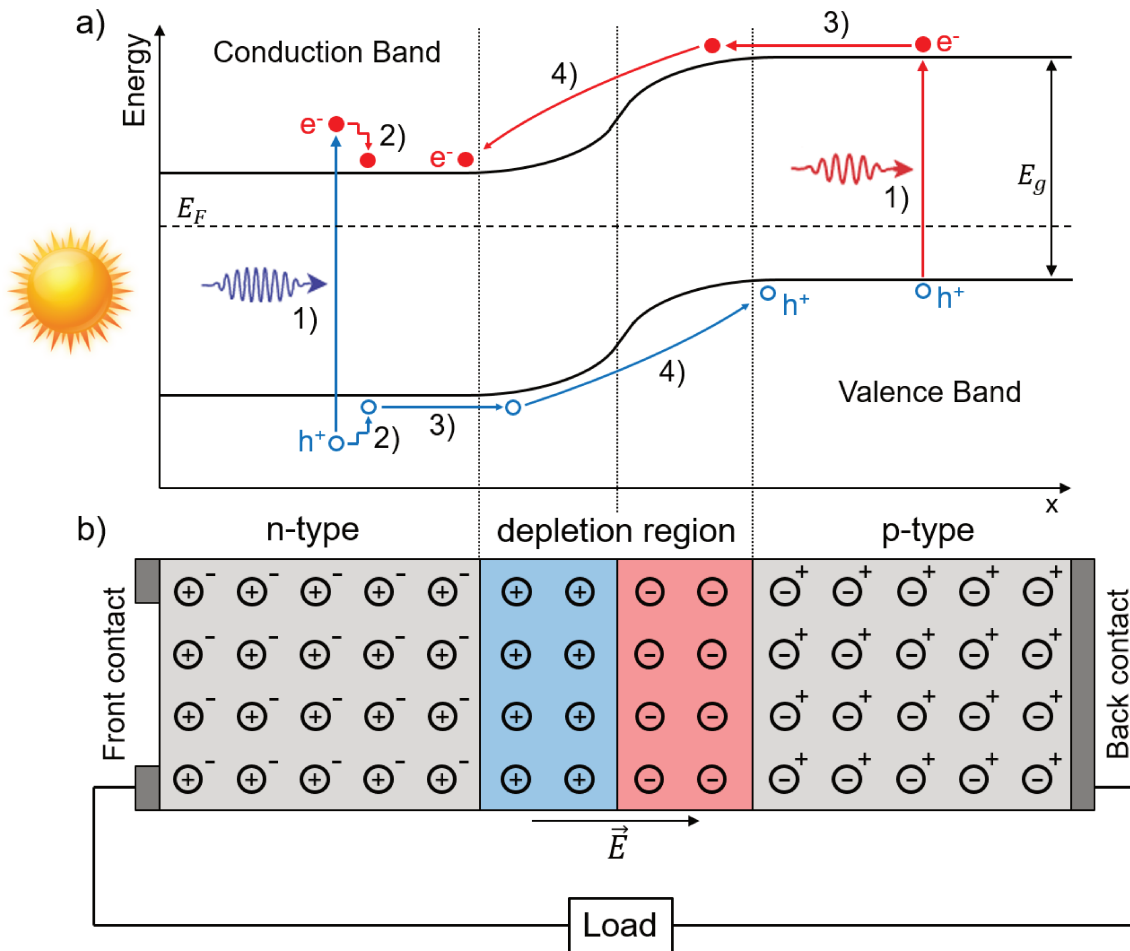


Fig. 1.7 a) Illustration of the solar cell operation principle using the band diagram of a p-n junction: 1) photons of energy above the bandgap, E_g , are absorbed and generate an electron (e^-)-hole (h^+) pair. Highly energetic photons, in blue, are absorbed close to the surface and low energy photons with just the minimum energy required, in red, are absorbed deeper in the material, 2) the excess of energy is loss by thermalization, 3) free electrons and holes can diffuse and reach the space charge region, 4) here the minority charge carriers are swept across the depletion region by the electric field, $\vec{E}$, where they become majority charge carriers. b) Scheme of a p-n junction where fixed charges, corresponding to the ion cores of the dopant atoms, are represented inside circles. In the depletion region there is no free carriers because the internal electric field, generated by the fixed charges, quickly sweeps free carriers out.

recombining is called the diffusion length, L , and it is related to the charge carrier lifetime, τ , through the diffusivity, D , following equation 1.2.

$$L = \sqrt{D\tau} \quad (1.2)$$

Since bulk recombination can only happen if both an electron and a hole are available, τ depends on the excess minority carrier concentration, Δn , respect to the equilibrium state, as described by the following equation:

$$\tau = \frac{\Delta n}{R} \quad (1.3)$$

where R is the recombination rate.

Any defects or impurities within or at the surface of the semiconductor increase recombination. Therefore, the recombination rate is usually high at the front and back surfaces where the lattice is disrupted and hence dangling bonds appear. Surface passivation, which consists of growing a layer on top of the semiconductor surface to tie up some of the dangling bonds, is used to reduce the Surface Recombination Velocity (SRV), a parameter that specifies the recombination rate at the surface.

In the bulk of the material, charge carriers recombine by either radiative, Auger or Shockley-Read-Hall (SRH) recombination. The bulk minority carrier lifetime, τ_{bulk} , can be then described by the following equation:

$$\frac{1}{\tau_{\text{bulk}}} = \frac{1}{\tau_{\text{radiative}}} + \frac{1}{\tau_{\text{auger}}} + \frac{1}{\tau_{\text{SRH}}} \quad (1.4)$$

In radiative recombination, which dominates in direct bandgap semiconductors, an electron from the conduction band directly combines with a hole in the valence band and releases a photon with an energy similar to the bandgap. Defect-mediated SRH recombination is a two-step process where an electron (or hole) is trapped by an energy state in the forbidden region which is introduced through defects in the crystal lattice. Finally, Auger recombination involves two electrons and a hole (or two holes and an electron). An electron and a hole recombine, but rather than emitting the energy as a photon, the energy is given to another electron in the conduction band (or to a hole in the valence band), which then thermalizes back down to the conduction band edge (or to the top of the valence band). Since this process is a 3-particle interaction, Auger recombination is most important at high carrier concentrations caused by heavy doping or high level injection under concentrated sunlight.

The p-n junction can prevent bulk recombination by spatially separating the electrons and holes through the action of the internal electric field, $\vec{E}$, existing at the depletion region.

When photo-generated minority carriers reach the p-n junction by diffusion, they are swept across the depletion region by the electric field where they become majority charge carriers. Therefore, electrons are swept to the n-type side of the junction, usually at the front surface, which becomes negatively charged and holes are swept to the p-type side at the back, which becomes positively charged, creating an electric potential difference or voltage. This phenomenon is known as the photovoltaic effect [10]. Upon connecting the front and back contacts through an external circuit, electrons flow creating an electric current which delivers power to the attached load. Finally, they are restored to the solar cell through the backside contact where they recombine with the holes, returning to the valence band with the same energy that they started with and completing this way the loop.

1.2.3 I – V curve of a single-junction solar cell

The solar cell performance is given by the electrical conversion efficiency, η , defined in equation 1.5 as the maximum electrical power produced by the solar cell, $P_{\max}$, divided by the total incident irradiance or light intensity, G , and the cell area, A . I_{MPP} and V_{MPP} are the current and voltage at the Maximum Power Point (MPP). The conversion efficiency can be then extracted from the measurement of the I – V characteristic, represented in figure 1.8, under some specific conditions, for example 1-sun of irradiance ($G^* = 1000 \text{ W/m}^2$), AM1.5G spectrum and 25°C .

$$\eta = \frac{P_{\max}}{G A} = \frac{I_{\text{MPP}} V_{\text{MPP}}}{G A} \quad (1.5)$$

The I – V curve of a solar cell is the superposition of a p-n diode I – V curve in the dark with the light-generated current [26]. Therefore, the current of an ideal solar cell under illumination can be described by equation 1.6.

$$I = I_L - I_0 \left[\exp \left(\frac{V}{n V_T} \right) - 1 \right] \quad (1.6)$$

Where I_L is the light-generated current or photocurrent, which is proportional to the number of absorbed photons and I_0 is the diode leakage current in the absence of light, known as the dark saturation current, which is influenced by recombination and thus is inversely related to material quality [27]. V is the applied voltage and $V_T = kT/q$ is the thermal voltage, with q the absolute value of electron charge, k the Boltzmann's constant and T the absolute temperature. The ideality factor n , assumed to be constant for simplicity, is a number typically between 1 and 2 and is a measure of the recombination type and location in a p-n diode. However, several recombination mechanisms with their corresponding ideality factors may

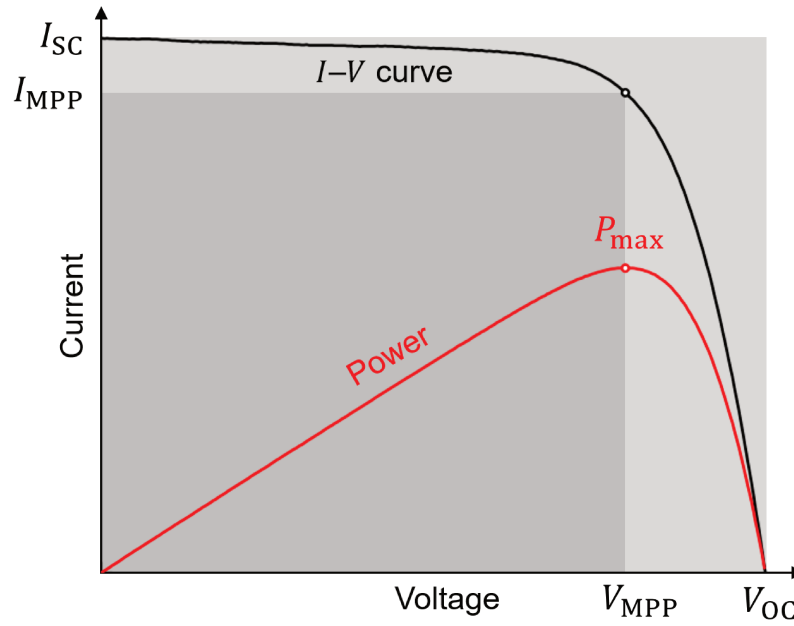


Fig. 1.8 I - V curve of a single-junction solar cell under illumination along with its power. The electrical parameters I_{SC} , V_{OC} , P_{max} and FF can be extracted from the I - V characteristic.

be present at the same time and therefore a convenient description may not always be possible in terms of a single exponential model.

In practice, resistive effects in solar cells reduce the conversion efficiency by dissipating power in parasitic resistances. Therefore, series resistance, R_S and shunt resistance, R_{SH} , are commonly added to the model, which is schematically shown in figure 1.9 and is mathematically described by equation 1.7. R_S are produced by current flowing through semiconductor and metal layers of limited conductivity and due to contact resistance. R_{SH} is typically due to manufacturing defects that provide an alternate current path for the photocurrent. The power losses due to R_S are more important for high I_L because, as stated by the Joule's first law, the ohmic losses are proportional to the square of the current. On the contrary, the effect of R_{SH} is particularly severe for low light levels because the fraction of current passing through the shunt is bigger.

$$I = I_L - I_0 \left[\exp \left(\frac{V + I R_S}{n V_T} \right) - 1 \right] - \frac{V + I R_S}{R_{SH}} \quad (1.7)$$

As shown in equation 1.8, the efficiency can also be expressed as a function of the short-circuit current, I_{SC} , the open-circuit voltage, V_{OC} , and the fill-factor, FF . All these

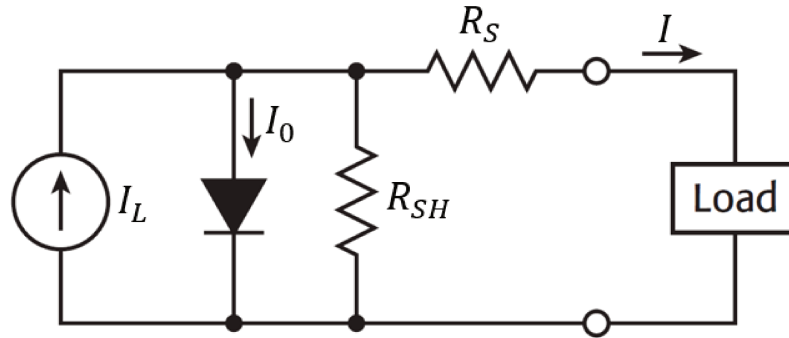


Fig. 1.9 Circuit diagram of a solar cell with series and shunt resistances. The current exits the device and power is delivered to the external load.

parameters can be determined from the I – V curve as seen in figure 1.8.

$$\eta = \frac{I_{SC} V_{OC} FF}{G A} \quad (1.8)$$

I_{SC} is the measured current when the voltage across the solar cell is zero, i.e. when the solar cell is short-circuited. I_{SC} can be approximated to the photocurrent I_L , as shown in equation 1.9, if series and shunt resistances are negligible, i.e. low R_S and high R_{SH} . The lower the bandgap the larger the I_{SC} , because more photons can be absorbed.

$$I_{SC} \approx I_L \quad (1.9)$$

V_{OC} is the voltage when the current is zero and it is a measure of the potential energy of the photo-generated carriers, which is limited by the material bandgap. Therefore, the higher the bandgap the higher the V_{OC} . As shown in equation 1.10, in which a negligible (i.e. high enough) shunt resistance is assumed, the V_{OC} can be expressed as a function of I_0 and I_L . Thereby, since I_0 depends on recombination, the V_{OC} is also a measure of the amount of recombination in the device.

$$V_{OC} \approx n V_T \ln \left(\frac{I_L}{I_0} + 1 \right) \quad (1.10)$$

The FF is defined by equation 1.11 and can be understood graphically as a measure of the “squareness” of the I – V curve. P_{max} , and hence also the FF , are strongly degraded if series resistance is high or if shunt resistance is low.

$$FF = \frac{P_{max}}{I_{SC} V_{OC}} = \frac{I_{MPP} V_{MPP}}{I_{SC} V_{OC}} \quad (1.11)$$

1.2.4 Efficiency limit

The fundamental efficiency losses using p-n junctions are due to transmission losses of low energy photons that are not absorbed and thermalization losses for absorbed photons, in which the excess energy above the bandgap is dissipated as heat. Therefore, the solar cell conversion efficiency is intrinsically limited by the bandgap of the p-n junction material. Low bandgap materials can absorb more photons and produce a high photocurrent, but the potential energy per charge carrier after thermalization is low. On the other hand, wide bandgap semiconductors will only absorb high energy photons generating a smaller current, but the potential energy per charge carrier after thermalization is high.

The maximum theoretical efficiency limit for p-n junction solar cells, commonly known as the Shockley-Queisser limit [28], can be calculated using detailed balance theory. This limit corresponds to the ideal case in which radiative recombination is the only mechanism for hole-electron recombination. In addition, the mobility of charge carriers is taken as infinite and it is assumed that all photons of energy equal or above the bandgap are completely absorbed. The detailed balance theory only takes into account fundamental limitations due to the laws of thermodynamics and semiconductor radiative processes. It consists in establishing that the number of electrons extracted from a cell per unit of time as electrical current is equal to the difference between the number of photons absorbed and those internally generated which are emitted from the device. The theoretical efficiency limit can be then obtained as a function of the bandgap. The Shockley-Queisser limit under 1-sun illumination for a single-junction solar cell is around 33% for a bandgap of 1.3 eV, which is close to the 1.12 eV of Si, [29–31].

However, Auger recombination, which is an important loss mechanism for c-Si solar cells at 1-sun illumination, as well as other intrinsic loss processes like parasitic free carrier absorption, are not taken into account in the Shockley-Queisser limit. A more empirical but less general approach, consists in choosing a particular device structure, like for example a Si p-n junction, and calculate its limiting performance from the known properties of Si as a function of some parameter like doping concentration or wafer thickness. Richter *et al.* [32] calculated a maximum efficiency of 29.4% for a 110 μm thick solar cell made of undoped Si based on state-of-the-art modeling parameters, taking into account an improved description of radiative and Auger recombination, updated optical properties of Si, free carrier absorption and the influence of bandgap narrowing.

As shown in figure 1.10 in blue, the current sc-Si solar cell efficiency record of 26.7% under 1-sun [33, 34] is already very close to this Si intrinsic upper efficiency limit, leaving very small room for further improvement. Conversion efficiencies of mc-Si and thin film

technologies are behind with records around 20%. The only emergent PV technology that has achieved a similar efficiency is perovskite solar cells, which have the advantage of using low-cost materials, but still suffer from instability problems. Multi-junction solar cells made of III-V semiconductors (compound materials including elements from the columns III and V of the periodic table) stand-out at the top of the chart with the highest conversion efficiencies.

1.2.5 Multi-junction solar cells

Multi-junction Solar Cells (MJSC), also known as tandem cells, are formed by stacking junctions, or subcells, with different bandgaps. MJSC allow to convert the broad solar spectrum more efficiently by using different adapted bandgaps for different spectral regions, as shown in figure 1.11a for a 2-junction (2J) solar cell with a Si bottom subcell. Since photons with energies below the bandgap are not absorbed, subcells in a MJSC can be vertically stacked in descending order of bandgaps, from the first on the front face with the wider bandgap, to the last on the back side with the shortest. Thereby, the more energetic photons are absorbed by the top subcell, while transmitted photons of lower energy can be absorbed by the next subcells as shown by the scheme in figure 1.11b.

Detailed balance theory can be applied to each of the individual junctions to finally add up the extracted power from each cell. For a 2J device with bandgaps of 1.6 and 0.9 eV the maximum efficiency under 1-sun is around 45% and it reaches 50% for a 3-junction (3J) with bandgaps of 1.9, 1.4 and 0.9 eV [30, 31]. As the number of junctions increases, the efficiency of the stack also potentially increases, but in reality semiconductor materials with an arbitrary bandgap and high quality do not exist. The current solar cell efficiency record of 46% [35, 34] is hold by a 4-junction stack under concentrated light equivalent to 508 suns, while the record efficiency at 1-sun is 38.8% for a 5-junction cell [36, 34]. The maximum possible photovoltaic conversion efficiency, corresponding to the limit case of an infinite ideal stack of junctions, is found to be 65.4% under 1-sun and 86.8% at the highest possible concentration [37, 30].

The subcells in a MJSC are usually manufactured by epitaxial growth from the same GaAs or Ge substrate, forming different layers and using tunnel junctions in between to connect them. This results in a 2-terminal (2T) configuration with the subcells connected in series, as shown in the left side of figure 1.11b. The overall device current of a series-connected MJSC is generally limited by the subcell with the lowest current, except in the cases where the limiting subcell presents low shunt resistance or low reverse breakdown voltage [38, 39]. Therefore, to optimize efficiency, the bandgaps have to be carefully selected so that the

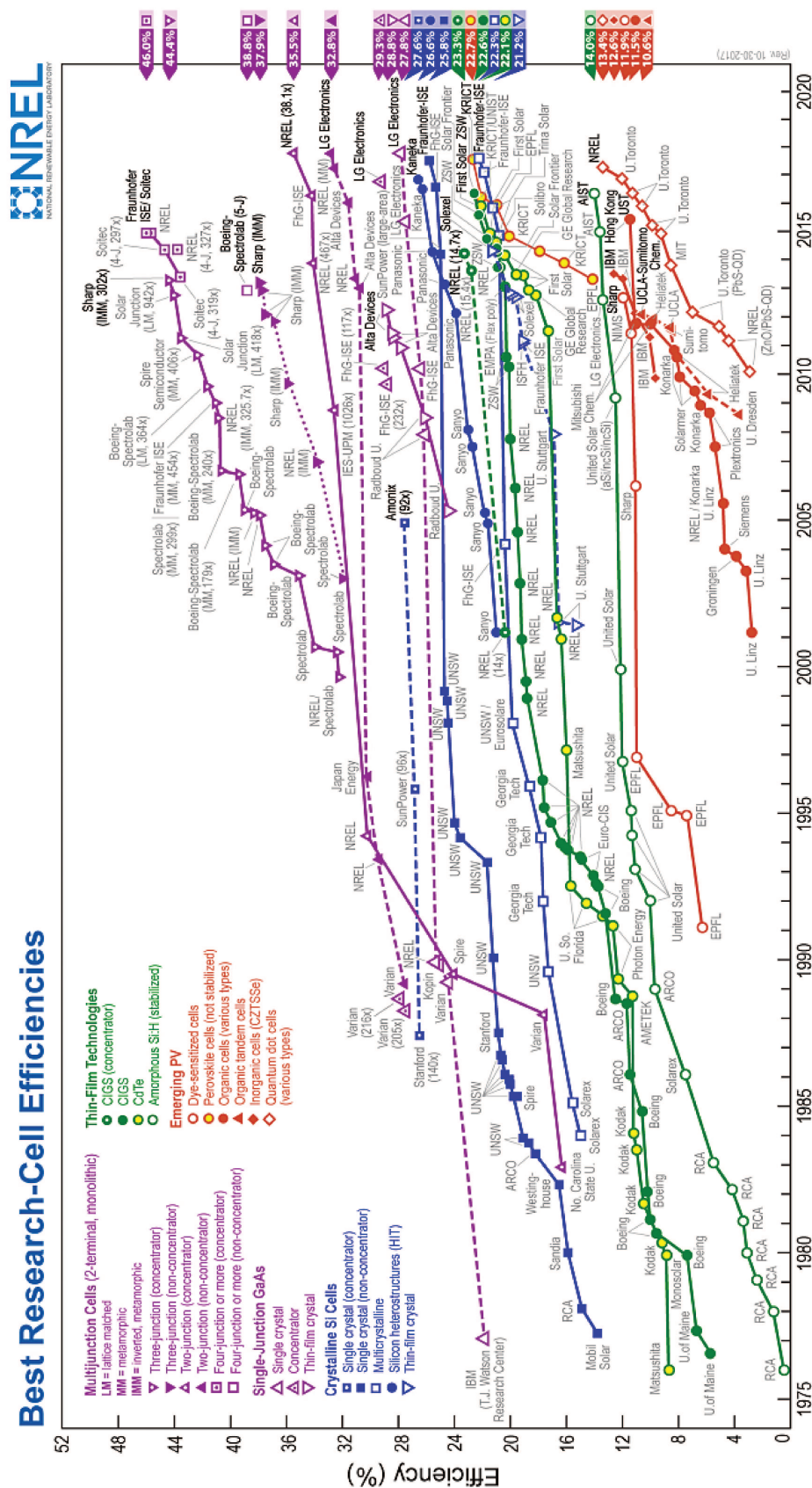


Fig. 1.10 History of best laboratory solar cell efficiencies for different PV technologies. Record conversion efficiency for Si solar cells (in blue) is 26.7%, while multi-junction solar cells (in violet) reach 46% under concentration. This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO.

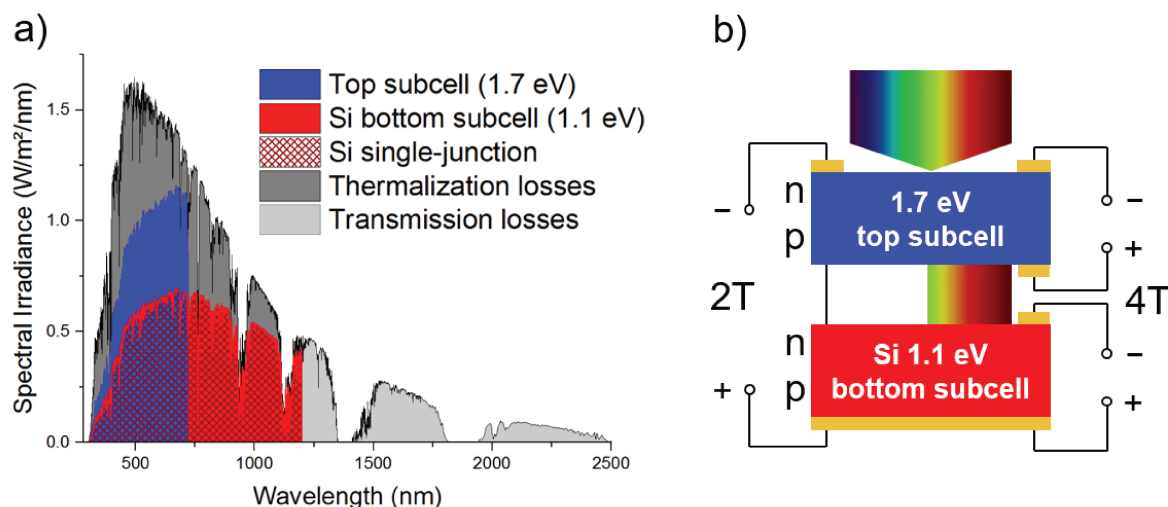


Fig. 1.11 a) Maximum portion of the AM1.5G spectrum that is possible to convert into electric power using a 2J solar cell with a top subcell of 1.7 eV and a bottom subcell made of Si, versus the available power for a Si single-junction cell. The absorption of high energy photons in the wide bandgap top junction reduces thermalization losses. b) Scheme of a 2J solar cell with a Si bottom subcell in series connected 2-terminal configuration or 4-terminal independent configuration.

subcells produce the same photocurrents, also known as current matching condition. This criterion severely limits the selection of bandgaps for optimal MJSC performance, although current matching can also be obtained by changing the junction thickness. Furthermore, as each subcell only absorbs light in a specific spectral region, the spectral irradiance has a strong impact on the subcell photocurrent ratios and hence on the overall current of the device, which makes series-connected MJSC very sensitive to spectral variations. In addition to monolithic MJSC manufactured by epitaxy, series connection is also the most common configuration for MJSC fabricated by mechanical stack techniques using metal interconnections, section 1.3.2.2, or wafer bonding, section 1.3.2.1.

On the other hand, current matching condition is not required in a 4-terminal (4T) configuration with the subcells operated independently, as shown in the right side of figure 1.11b. Therefore, the performance is less sensitive to the spectrum, which leads to an increase in the annual energy yield (AEY: the ratio of the total energy produced during one year over the total incident irradiance) [40, 41]. In addition, near optimal performance can be achieved for a wider selection of bandgaps. Mechanically stacked cells with transparent adhesives that electrically isolate the subcells, section 1.3.2.2, commonly use a 4T configuration.

However, it should be noted that in a 4T configuration there are module level issues in order to reduce mismatch losses produced by cells operating at different currents and voltages,

such as the need of more inverters and wire or the operation of independent loads, which increases the complexity. On the contrary, 2T configuration is very attractive in this regard because the cells can be easily incorporated into the standard Si single-junction module technology.

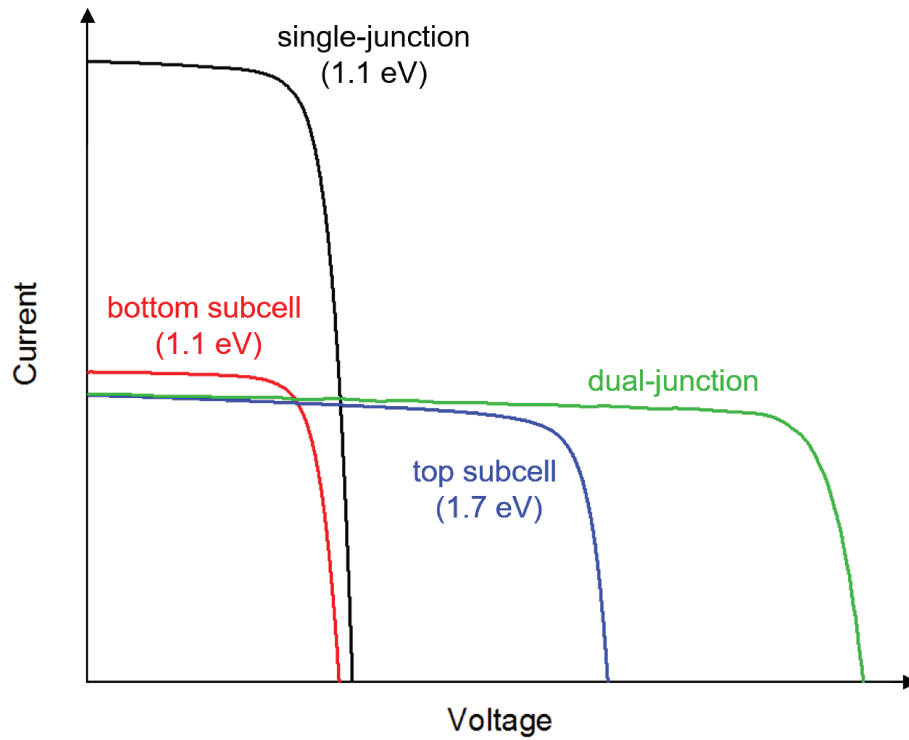


Fig. 1.12 I – V curves under illumination of a 2J solar cell together with the individual top and bottom subcells that form it, compared to a bottom subcell as a standalone single-junction. In this example, the subcells are not perfectly current matched and thus the I_{SC} of the dual-junction is limited by the lower current of the top subcell. The V_{OC} is the sum of the individual subcell voltages.

In series-connected MJSC, the individual I – V characteristics of each subcell combine to produce the I – V curve of the whole device. An example is shown in figure 1.12. In general, for an appropriate combination of bandgaps, the absorption of the solar spectrum is equally divided between the subcells and thus the photocurrent produced by each subcell in the MJSC is lower than in the case of a single-junction made with the same material as the bottom subcell. Since the subcell generating the smaller photocurrent limits the total device current, the I_{SC} of a MJSC is also generally lower than that of a single-junction. Conversely, the V_{OC} of series-connected MJSC is higher because it is the result of summing up all the individual subcell voltages. Therefore, MJSC deliver electric power at higher voltage and lower current, which is an advantage because it reduces series resistance losses.

Despite the incredible potential and the impressive efficiencies that have been already achieved, MJSC are very expensive, notably due to the expensive Ge and III-V substrates needed. Therefore its market, accounting for less than 1% of the total PV production, is restricted to space applications or high concentration PV used in certain sunny areas with high values of direct normal irradiance, further explained in section 1.2.6. Researchers and industry are therefore increasing their interest in new technologies capable of achieving higher efficiencies while maintaining moderate production costs. The use of wide bandgap III-V (or perovskite) junctions stacked on top of Si solar cells, section 1.3, is a promising approach to overcome the Si single-junction efficiency limit while keeping at the same time the advantages of a well-established and mature Si industry using widely available Si wafers. Moreover, such tandem solar cells may operate under low concentrated sunlight, allowing to use smaller cell areas, thus reducing the materials and production costs. Si-based tandem cells are expected to appear in mass production operations by 2020 with 5% market share by 2028 [19].

1.2.6 Concentrated photovoltaics

Solar cells may operate under concentrated sunlight using lenses or mirrors of large area to focus direct irradiance onto a small MJSC, usually below 1 cm^2 . The ratio between the optics area to the solar cell area defines the concentration level, X , which is dimensionless by definition. However, by tradition it is often expressed in units of *suns* [42]. The key principle of Concentrated PV (CPV), is the use of cost-efficient concentrating optics that reduce the area of the more expensive and highly efficient MJSC. Cost reduction is then possible by replacing expensive III-V MJSC with cheaper optics. Concentration factors in High Concentrated PV (HCPV) are higher than 300 suns and usually primary and secondary optics are needed, which adds complexity to the system. As shown in figure 1.13, double-axis tracking mechanisms, known as sun-trackers, are also required to keep the light focused on the solar cells as the Sun moves through the sky. HCPV can be cheaper than conventional flat-plate PV, in terms of LCOE, in some very hot locations with high direct normal irradiance [43].

Since new concepts of potentially low-cost and highly-efficient MJSC are being developed, like the III-V on Si approach presented in section 1.3, Low Concentration PV (LCPV) could be used to simplify the architecture of a typical HCPV system. In LCPV the concentrations are below 100 suns and therefore only primary optics, a passive heat sink and a single-axis tracker are needed. Low concentration offers wider angular misalignment acceptances, which implies the use of less accurate and hence cheaper sun-trackers than

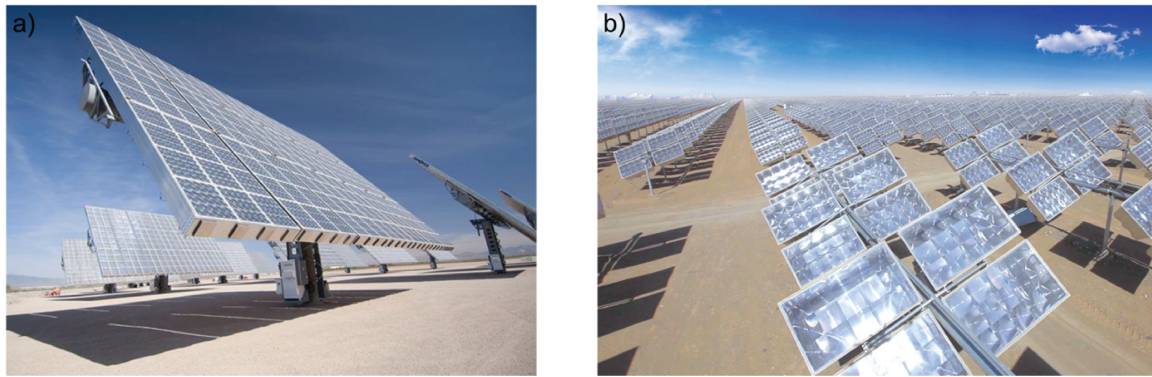


Fig. 1.13 HCPV systems using double-axis sun-trackers and Fresnel lenses to concentrate sunlight, a) Amonix system with a concentration factor of 500 suns, b) Suncore 60 MW plant in China.

for HCPV. Examples of LCPV systems using aluminum mirrors to concentrate the light are shown in figure 1.14. In these LCPV systems, each mirror concentrates the sunlight on the back side of the adjacent mirror where the cells are positioned. The aluminum mirror then combines the functions of primary optics, mechanical cell support and heat sink.

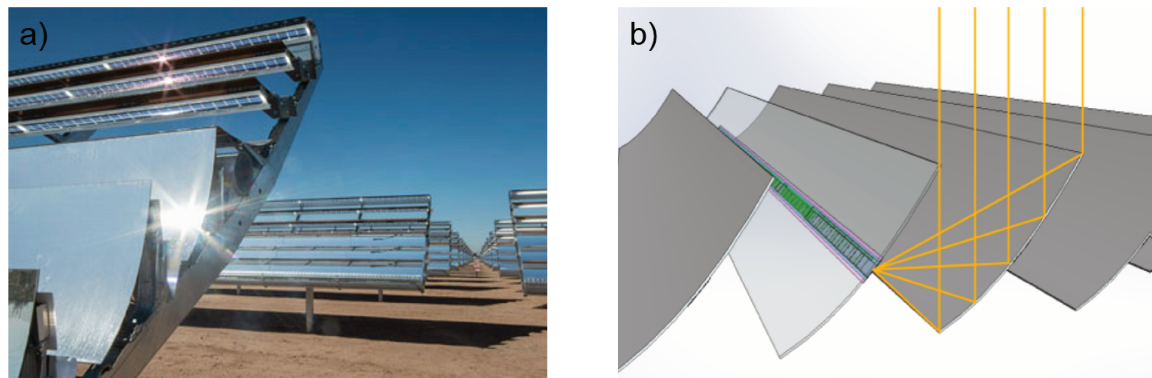


Fig. 1.14 LCPV systems using aluminum mirrors to concentrate the light, a) Sunpower commercial LCPV system with a concentration factor of 7 suns, b) LCPV highly integrated system with a concentration factor of 15 suns [44].

In addition to the benefit of reducing the solar cell area, conversion efficiency generally increases with concentration. Since the photocurrent is proportional to the incident light intensity, I_{SC} can be approximated to a linear function of X , as long as series resistances are not too high:

$$I_{SC}(X) \approx X \cdot I_L^* \approx X \cdot I_{SC}^* \quad (1.12)$$

where I_L^* is the photocurrent at 1-sun. However, the efficiency is not affected by the I_{SC} linear increase, in the numerator of equation 1.8, because it is compensated by the also linear increase of the incident light intensity, $G(X) = X \cdot G^* = X \cdot 1000 \text{ W m}^{-2}$, in the denominator:

$$\eta(X) \approx \frac{X I_{SC}^* V_{OC}(X) FF(X)}{X G^* A} \quad (1.13)$$

The concentration efficiency boost is therefore the result of an increase in V_{OC} , which also produces a slight increase in the FF . Combining equations 1.10 and 1.12, $V_{OC}(X)$ is found to increase logarithmically with concentration:

$$V_{OC}(X) \approx V_{OC}^* + n V_T \ln(X) \quad (1.14)$$

In practice, the efficiency increase with concentration is limited by the effect of series resistance causing a FF drop together with a V_{OC} increase lower than that predicted by equation 1.14. Accordingly, for a given value of R_S , there is a maximum efficiency achievable at an optimum concentration level, X_{opt} , that can be approximated by equation 1.15 [45]. In figure 1.15, the effect of concentration in a 4-junction solar cell is shown. It can be observed that the maximum efficiency of 44.7% is obtained for a $X_{opt} = 297$ suns [46].

$$X_{opt} \approx \frac{n V_T A}{R_S I_{SC}} \quad (1.15)$$

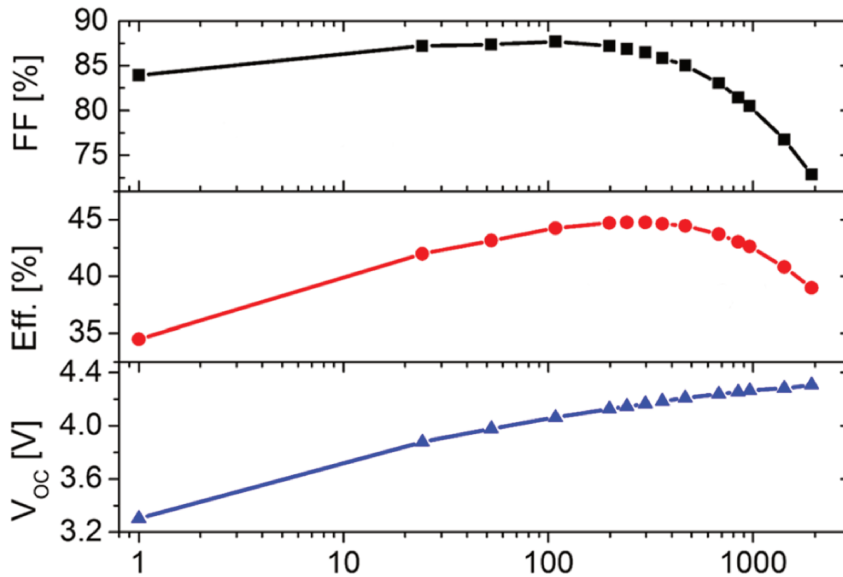


Fig. 1.15 Effect of concentration on the electric parameters of a 4-junction solar cell [46].

1.3 III-V on Si tandem solar cells

In the previous sections, the basic principles of solar cell operation and the context of PV were discussed, highlighting the imminent entry of Si-based tandem cells into the market. In this section, III-V on Si MJSC are presented, giving a state-of-the-art overview of the different manufacturing approaches and the most remarkable realizations reported in the literature.

MJSC combining wide bandgap III-V top subcells with a Si bottom cell offer the potential to overcome the 33% single-junction efficiency limit while taking advantage of the global investment that has been made in Si PV manufacturing. Despite the great efficiencies of III-V MJSC, the dominance of Si solar cells and their plummeting prices in the recent years have made it challenging for other technologies to make a strong commercial impact. Therefore, III-V on Si PV is a promising way for reducing the LCOE, thanks to the unification of both III-V high efficiencies with low-cost and widely available Si substrates [47, 48]. In addition to the substantial cost benefits associated with the larger-area, and lower-cost of Si substrates, Si also offers higher thermal conductivity and superior mechanical strength in comparison to GaAs or Ge substrates [49].

As shown by detailed balance modeling, figure 1.16a, Shockley-Queisser limit conversion efficiency of 45% under 1-sun is already obtained for 2J based on Si with a top subcell bandgap of about 1.7 eV [50]. As already explained in section 1.2.5, this bandgap criterion can be relaxed in the case of independently operated subcells because the current matching condition is not required. The maximum efficiency for a 3J solar cell with a Si bottom subcell is found to be over 50% using a top subcell of about 2.0 eV and a middle subcell of 1.5 eV, 1.16b.

Manufacturing of III-V on Si MJSC can be done by heteroepitaxial growth of the III-V layers using the Si bottom subcell as the substrate, known as monolithic approach, or by stacking independently grown III-V subcells on top. The stacking approach can be done by mechanical stack or wafer bonding techniques and requires expensive GaAs or Ge substrates in order to grow the III-V subcells. Therefore a substrate reuse technique has to be implemented in this case in order to keep down the manufacturing costs. In the next sections, the different fabrication techniques will be reviewed, together with the most important achievements reported in the literature.

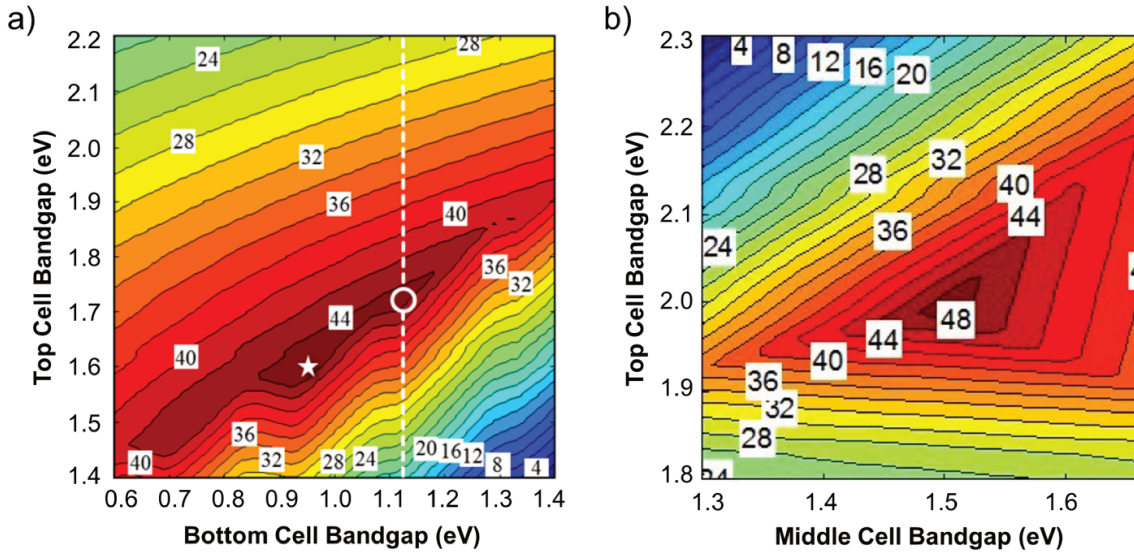


Fig. 1.16 Theoretical maximum solar cell efficiency contours in the Shockley-Queisser limit under 1-sun AM1.5G spectrum, a) for a 2J solar cell, in which the global maximum is marked by the star and the dashed line with circle indicates the fixed Si bottom subcell bandgap of 1.12 eV and its associated local maximum [50] and b) for a 3J as a function of the top and middle subcell bandgaps given a 1.12 eV bottom subcell [51].

1.3.1 Epitaxial growth of III-V on Si

Epitaxial growth of high quality III-V semiconductors on Si substrates remains the “holy grail” in the search for cost effective optoelectronic devices, including highly efficient solar cells. As shown in figure 1.17, the large lattice parameter mismatch, or misfit, between Si and all semiconductor compounds having optimum bandgaps is one of the main reasons why it is so difficult to grow high quality III-V materials directly on Si. Other important problems are the 60% mismatch in coefficient of thermal expansion that can cause cracks and the nature of polar/non-polar material interfaces that produce anti-phase domains, stacking faults and twins [52, 51].

If the thickness of the III-V epitaxial layer, or epilayer, is small, the misfit causes a strain where the in-plane crystal lattice compresses to conform to the smaller lattice of the Si substrate while the out-of-plane crystal bonds stretch away from the equilibrium lattice spacing in response to the in-plane elastic deformation [52]. The energy associated with the strain is proportional to the thickness of the epilayer. At some critical thickness it becomes energetically favorable for some of the bonds in the lattice to break. These defects in the crystal structure propagate to the surface of the film and are known as threading dislocations. The formation of dislocations and the change of the epilayer’s crystal lattice constant to its equilibrium value is known as relaxation and defines the metamorphic growth regime.

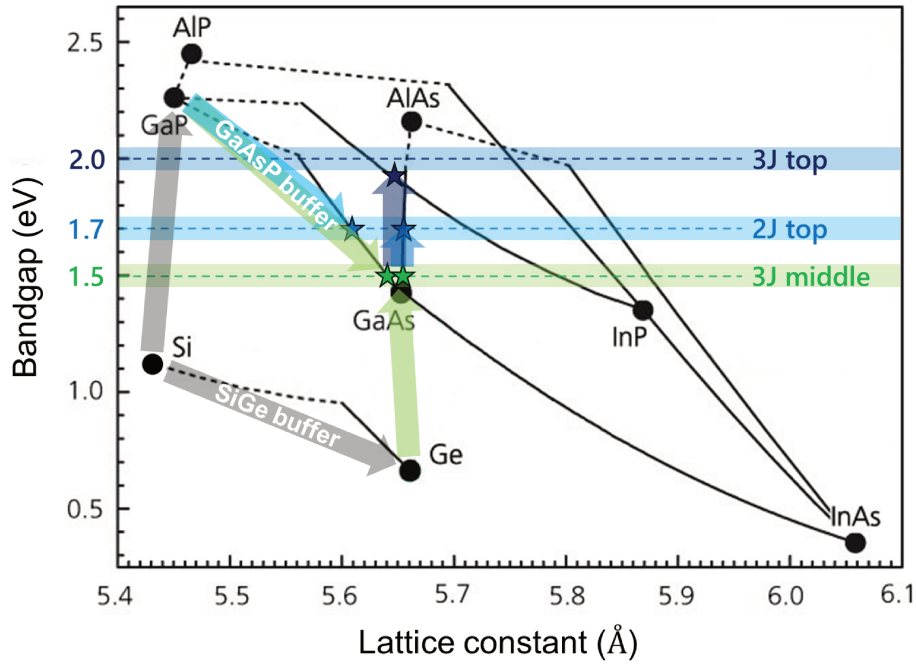


Fig. 1.17 Semiconductors and binary compounds, represented by black dots, arranged according to its bandgap and lattice constant. Black lines are ternary combinations. The optimum bandgap configurations for 2J and 3J III-V on Si cells are highlighted. Arrows represent lattice-matched grow paths leading to optimum bandgaps marked with a star.

The extent of this relaxation depends on many factors including the amount of misfit, layer thickness, and growth temperature. Threading dislocations can extend through the device causing partial short circuiting of p-n junctions and degradation of optical and electrical properties due to electronic defect states that act as recombination centers in the active layers of the solar cell, reducing this way the charge carrier's lifetime. Threading Dislocation Density (TDD) above 10^5 cm^{-2} have already major impact on device performance [53].

1.3.1.1 Lattice-mismatched epitaxy of GaAs on Si

The direct epitaxial growth of GaAs on Si, with a 4% lattice parameter mismatch, results in extremely large TDD, on the order of 10^9 cm^{-2} or higher [51]. In the '80s and '90s, much effort was invested in reducing TDD of (Al)GaAs epilayers grown on Si [54–56]. The best results, 21.2% efficiency under AM0 spectrum for a 2T 2J solar cell [57], were obtained using an AlGaAs buffer and thermal cycle annealing, which causes the conversion of threading dislocations, that propagate to the surface, to harmless dislocations parallel to the growth plane, thus improving the quality of the epilayer. However, the high TDD values of around 10^7 cm^{-2} still limited the device performance. Furthermore, due to the strong bond formed

between oxygen and aluminum, oxygen contamination during the growth of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers induces defects and hence reduces minority carrier lifetime [58, 59].

1.3.1.2 Metamorphic graded buffer

Another way to reduce TDD in III-V epilayers grown on Si is the use of metamorphic graded buffers in which composition gradually changes. The role of the buffer layer is to gradually change the lattice constant, starting from the Si substrate to finally reach the target lattice constant of the III-V material. As shown in figure 1.17, $\text{Si}_{1-x}\text{Ge}_x$ and $\text{GaAs}_x\text{P}_{1-x}$ are the two possible grow paths. Above these buffers, the p-n junction active layers can be grown lattice matched. Although dislocations are present in the buffer layer, this has no impact on the recombination of minority charge carriers because they are located in an inactive region far away from the p-n junction and therefore only majority carriers pass through. However, due to the considerable thickness that is often required, this layer could have an impact in the series resistance of the device and thereby a thin buffer layer is preferred.

$\text{Si}_{1-x}\text{Ge}_x$ graded buffer can be used to modify the lattice parameter of Si to GaAs by gradually increasing the germanium concentration from 0 to 100%. This way high-quality relaxed Ge layers can be grown on a Si substrate with a TDD as low as 10^6 cm^{-2} , providing a “virtual” Ge platform for subsequent GaAs growth [60–63]. However, germanium has a lower bandgap than Si and therefore the $\text{Si}_{1-x}\text{Ge}_x$ buffer eliminates the possibility of using the Si substrate as a bottom subcell because it does not provide the optical transparency needed. An interesting novel approach consists in forming an active subcell on the graded $\text{Si}_{1-x}\text{Ge}_x$ buffer. A GaAsP/SiGe 2J solar cell has been recently reported showing an efficiency of 18.9% under AM1.5G spectrum [64].

On the other hand, $\text{GaAs}_x\text{P}_{1-x}$ buffer approach provides light transmission to the bottom Si subcell because the GaP bandgap is larger than that of Si, thereby allowing a tandem cell with a standard active Si bottom subcell. First, a GaP nucleation layer is grown on the almost lattice-matched Si substrate. Then, the $\text{GaAs}_x\text{P}_{1-x}$ buffer is grown by gradually increasing the arsenic concentration until reaching the optimum bandgap for the top cell [65, 66, 50, 67, 68]. However, as shown in figure 1.18, the high TDD of around 10^7 cm^{-2} still limits the performance, being 19.7% the best conversion efficiency for a 3J GaInP/GaAs/Si [69, 34]. Furthermore, the high temperature during the III-V epitaxy on Si, typically around 700°C for a few hours, can cause degradation of minority carrier lifetime in the Si bottom subcell [70].

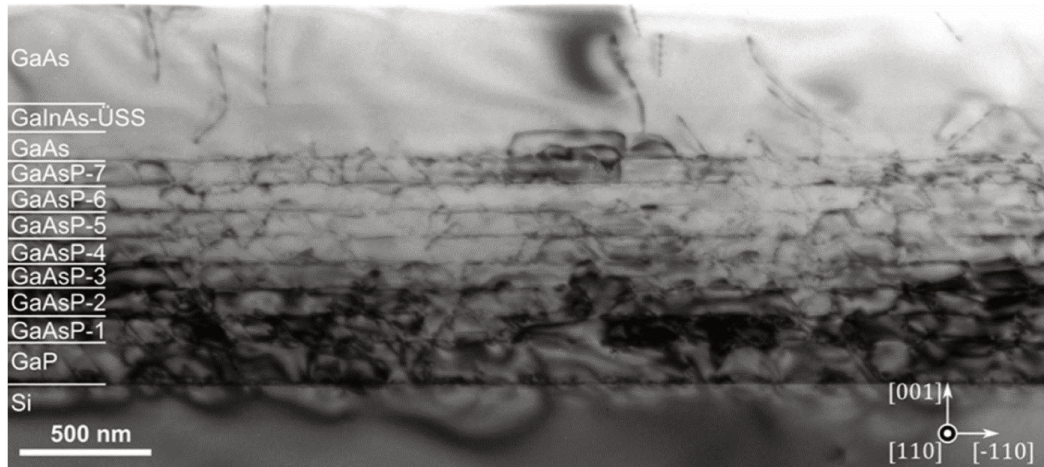


Fig. 1.18 TEM image of a $\text{GaAs}_x\text{P}_{1-x}$ metamorphic graded buffer on Si where a high TDD is visible [69].

1.3.1.3 Lattice-matched epitaxy of GaAsPN on Si

Finally, the quaternary alloy GaAsPN has been recently studied because it is lattice matched with Si and has a bandgap energy close to 1.7 eV, which is optimum for a 2J tandem cell based on Si [71–75]. This approach is very attractive as it offers the opportunity to overcome the apparition of threading dislocations. The first reported tandem solar cell made of $\text{GaAs}_{0.10}\text{P}_{0.86}\text{N}_{0.04}$ (1.8 eV) presented an efficiency of 5.2% [76]. The reason for this bad conversion efficiency is the low quality of the GaAsPN material that presents defects and unintentional impurities which degrade the carriers lifetime. In addition, further improvement on GaAsPN doping is required to make possible an optimized tunnel junction.

1.3.2 III-V on Si stack

A good option to avoid hetero-epitaxy issues consists of joining independently processed Si and III-V solar cells by direct wafer bonding or mechanical stack techniques. This way, III-V top cells can be grown lattice matched on GaAs or Ge substrates with good crystal quality. However, due to the high cost of these substrates, this approach has to be combined with substrate reuse strategies like epitaxial lift off or spalling in order to be cost competitive [77]. In addition, for 2T solar cell operation, a low resistance interconnection between the top and bottom subcells is required to avoid adding series resistance.

1.3.2.1 Wafer bonding

“Direct wafer bonding” refers to the phenomenon that mirror-polished, flat, and clean wafers of almost any material, when brought into contact at room temperature, are locally attracted to each other by weak Van der Waals or hydrogen-bridge forces and spontaneously adhere or “bond” to each other. Afterwards, annealing is usually required to consolidate the bonding and to increase the number of covalent bonds, which are one or two orders of magnitude stronger [78].

The main application for PV is the manufacturing of high quality crystalline layers regardless of the possible polar/non-polar and lattice parameter mismatches with the substrate, avoiding this way epitaxial growth related problems. The fabrication process flow of a III-V on Si tandem solar cell by wafer bonding is shown in figure 1.19. The III-V top subcell is grown inverted by Metalorganic Vapor Phase Epitaxy (MOVPE) on a GaAs substrate and is then bonded to a Si bottom subcell, which is fabricated independently. Afterwards, the GaAs substrate is removed, followed by the deposition of the metal contacts, the mesa etching to partially isolate the individual cells and finally the ARC deposition. As will be explain in section 1.3.2.3, the expensive GaAs substrate should be reused in order to make this approach economically viable.

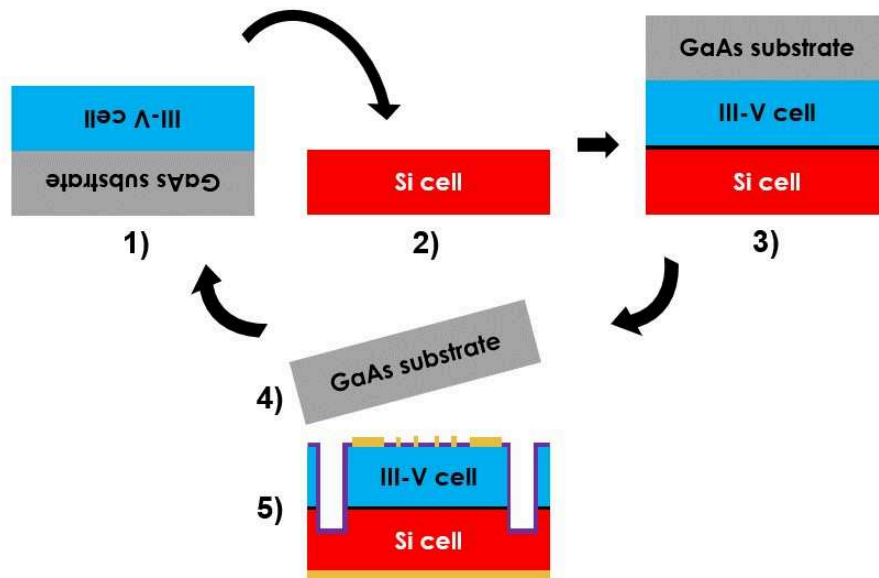


Fig. 1.19 Fabrication process flow for a wafer bonded III-V on Si tandem solar cell: 1) the III-V top subcell is grown inverted on a GaAs substrate, 2) the Si bottom subcell is fabricated independently, 3) the GaAs and Si subcells are bonded together, 4) the GaAs substrate is removed, 5) the final cell processing is done.

Wafer bonding is not only used for III-V on Si tandem solar cells, for example the bonding of InP and GaAs, developed by Soitec, CEA-LETI and Fraunhofer-ISE, allowed the manufacturing of a 4-junction cell with a record efficiency of 46.0% at a concentration factor of 508 suns [69, 34], which is the most efficient solar cell to date.

In contrast with metal interconnection or adhesive mechanical stack techniques, direct wafer bonding does not require any additional material or metal interfacial layer, which assures the transparency of the interface, allowing to use the Si substrate as an active junction. The surface morphology of the two wafers is one of the main challenges, as particles and local areas with high surface roughness cause voids at the wafer-bonded interface. Therefore, the bonding process has to be done in a clean room environment and only especially designed Si cells with planar front sides can be used, often requiring additional Chemical-Mechanical Polishing (CMP) of their surfaces.

The first step of the direct wafer bonding process consists then on preparing the surfaces. Different bonding techniques can be classified depending on the surface preparation. In chapter 2 a review of the different wafer bonding approaches for the manufacturing of tandem solar cells is done.

Outstanding results have been recently reported for a 2T 3J GaInP/GaAs//Si solar cell manufactured by Surface Activated Bonding (SAB), showing 33.3% conversion efficiency under 1-sun [79]. Using SAB technique highly conductive and transparent bonding interfaces have been demonstrated. However, ultra-high vacuum conditions and ion beam sputtering are required. Mechanical stack approach, discussed in the next section, has not these constraints.

1.3.2.2 Mechanical stack

The great advantage of mechanically stacked cells is the possibility of using the best solar cells already developed, with the optimum bandgaps, and “simply” connect them together through the metal grids or using a transparent adhesive. As an example, mechanical stacking enables the easy integration of a Si bottom cell with front side texturing, which is not possible in epitaxial or wafer bonding approaches. Moreover, they do not require a tunnel diode between the subcells, which reduces the complexity of the top cell growth process.

In order for the top cell to be transparent to sub-bandgap photons that are intended to be absorbed by the bottom, it has to include some specific design features like a polished back surface with an Anti-Reflection Coating (ARC), grid back contacts aligned with the front grid and a substrate-free design to reduce parasitic absorption. The disadvantages are the optical losses due to reflection at the interfaces and the shadowing caused by the metallic

interconnection grid. The use of an interlayer with a high refractive index and adapted ARC can reduce these losses.

When a **transparent adhesive** is used, the top and bottom subcells must be operated independently in a 4T configuration because the adhesive is usually nonconductor and therefore the subcells are isolated. On the contrary, the direct metal interconnection between the top cell back side grid and the bottom cell front side grid enables a 2T configuration.

Impressive results have been reported recently for mechanical stacked 2J GaAs//Si and 3J GaInP/GaAs//Si solar cells, with 1-sun conversion efficiencies of 32.8% and 35.9% respectively in a 4T configuration [80, 48]. A thin layer of optically transparent and electrically insulating epoxy is used to attach the top cell onto a glass slide. The glass slide acts as support for the thin III-V top cells during its processing and allows a completely separate fabrication of the top and bottom cells until they are glued together using another layer of epoxy. Metal grid lines at the front and back sides of the top cell are aligned and an ARC on both the front and back sides was deposited in order to reduce shadowing losses. A scheme of the structure is shown in figure 1.20a.

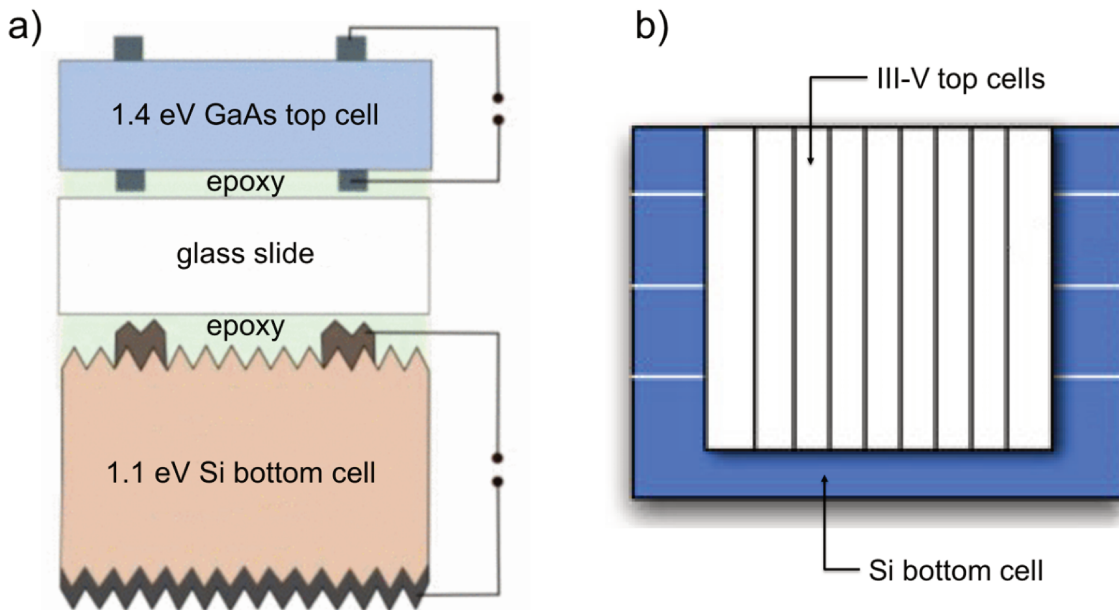


Fig. 1.20 a) 4T 2J GaAs//Si solar cell fabricated with transparent adhesive [80, 48]. b) Top view of a 2T III-V on Si solar cell fabricated by metal interconnection using the areal current matching concept in which the area of the III-V top subcells is smaller than the Si bottom subcell [81].

An interesting 2T **metal interconnection** design was presented [81], which consists in an areal current matching approach, thereby avoiding top subcell bandgap and thickness

constraints usually required to obtain current matching condition. In this technique, instead of thinning the top subcell to reach current matching, its area is reduced. Therefore, the top GaInP/InGaAs cells have a smaller area than the Si bottom cell, exposing it to the full solar spectrum and increasing this way its photocurrent. Top view of the structure is shown in figure 1.20b. A conversion efficiency of 25.5% under 1-sun was reported. This technique was also combined with a Palladium (Pd) nanoparticle array-mediated mechanical stack to fabricate a GaInP/GaAs//Si solar cell [82].

1.3.2.3 III-V substrate reuse

III-V on Si solar cells manufactured by wafer bonding and mechanical stack approaches require expensive GaAs substrates to independently grow the III-V junctions. A possible way to make these approaches economically viable is to reuse the substrate many times, thus spreading its cost across many cells. The two main substrate reuse strategies are Epitaxial Lift-Off (ELO) and spalling. ELO is the most mature, with small-scale manufacturing operations already underway, while spalling is still in development and good performances have only been demonstrated in the laboratory.

Thin film solar cells enabled by substrate reuse strategies have also the advantages of being flexible and lightweight, with a very high power-to-weight ratio, which is useful for new PV applications like for example Unmanned Aerial Vehicles (UAV) or electric cars.

Epitaxial Lift-Off (ELO) refers to a technique that exploits the selective wet etching chemistry of certain III-V compounds, allowing to remove a thin release sacrificial layer grown between the wafer and the cell structure. The released III-V cell can be used this way in combination with the Si bottom cell and the III-V wafer can be reused for subsequent epitaxial growths [83]. As early as 1978, the extreme etch selectivity of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ relative to GaAs in hydrofluoric (HF) acid, in which $\text{Al}_x\text{Ga}_{1-x}\text{As}$ is etched around 100 times faster than GaAs, allowed to remove GaAs films from their parent substrates [84]. The etching rate of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ depends on the aluminum fraction, which is often higher than 0.7. The main problem with any of these etching processes is the need to circulate the reactants and the reaction products in and out of the small crevice formed between the film and the substrate. Therefore, etching of the thin release layer tends to be mass-transport limited and a very long process.

A novel approach was presented in 1987 where the surface of the epitaxial film was covered with Apiezon black wax [85]. The wax imparts a compressive stress to the film which causes it to curl and lift, opening up the etch front as the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ release layer is removed and allowing the etch to continue. This lifting action increases the diffusion

of etchant to the active etching regions and take reaction products away. A decade after, crack-free films as large as 20 cm^2 (a full 2" substrate) were obtained by ELO [86] with lateral etch rates up to 30 mm/h [87]. This was achieved by forcing the slit to open with a constant radius of curvature by guiding the foil and the part of the film that is separated over a curved surface as shown in figure 1.21a. In this way, the curvature of the film necessary to enhance the etching rate and the reliability of the process, do not depend on the variable tension of the wax but on the controlled applied force. A metal film between the structure and the wax counteracts some of the tension preventing crack formation in the thin film.

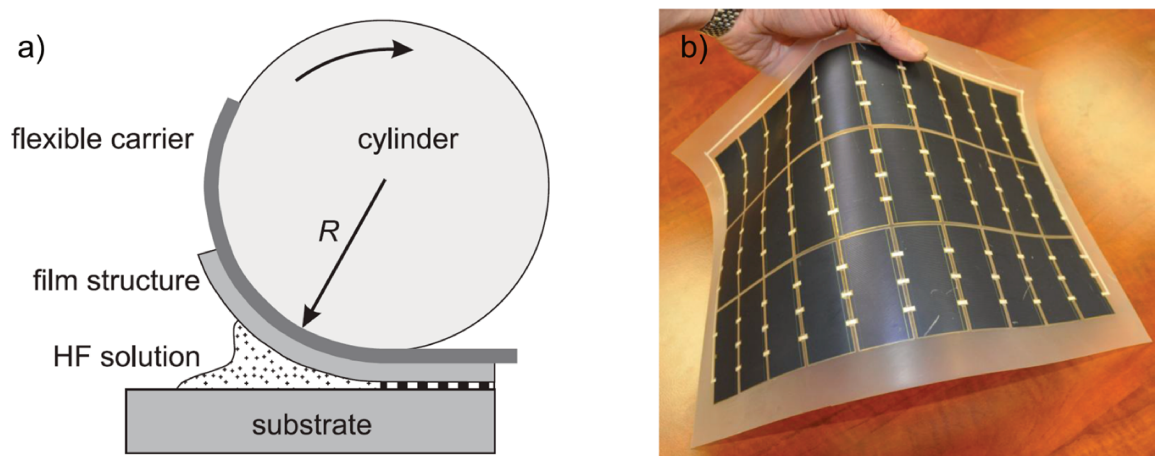


Fig. 1.21 a) Schematic representation of the ELO process with a stabilized radius of curvature by guiding the temporary flexible carrier over a cylinder surface [87], b) Flexible solar sheet consisting of an array of 30 interconnected large-area GaAs ELO solar cells manufactured by MicroLink Devices [88].

High performance devices can be manufactured using ELO, like the current 28.8% 1-sun efficiency record for a III-V single-junction cell, hold by Alta Devices [89, 34], and the recently 37.7% 1-sun conversion efficiency announced by MicroLink Devices for a 3J thin film solar cell [90]. MicroLink Devices have developed an industry-first ELO process capable of lifting off large areas of semiconductor material (6" for GaAs substrates and 4" for InP substrates), as shown in figure 1.21b, without any degradation of material quality or performance characteristics, proving that ELO is finally transitioning to a viable manufacturing technology [88, 91]. Although still being a long process, requiring approximately 12 hours to complete, ELO is amenable to batch processing, which enables scaling up of the process to lift off hundreds of substrates within a 24-hour period. After the ELO process has been performed, the original substrate is restored to epi-ready quality using a short CMP. The number of possible reuses is limited primarily by the 40 to $10\text{ }\mu\text{m}$ of material removed during repolishing. However, potential cost reduction resulting from substrate reuse is limited rather

by the costs that are incurred in each cycle to prepare the substrate for another epitaxial deposition [77].

IBM also works in this field and presented a new etching ELO process where AlAs-based sacrificial layer is replaced with phosphide-based materials (InGaP, InAlP or InP) and HF etchant is replaced by HCl [92]. This new method minimizes the amount of post-etching residues and keeps the surface smooth, leading to direct reuse of the GaAs substrate without the need of post-processing steps to restore the epi-ready condition, like CMP or chemical etching, or extra epitaxial protection layers. After the etching process, the parent wafer only needs to be rinsed thoroughly and then cleaned with a standard wafer cleaning procedure before the next epitaxial growth. HCl as an etchant also poses significantly lower risks compared with highly lethal and corrosive HF. These attributes makes the new ELO process much safer and economically viable for manufacturing compared with the conventional HF method.

Controlled spalling is another recently developed substrate reuse approach based on fracture mechanics. It allows near room temperature kerf-free layer removal at a precise depth parallel to the substrate surface. A scheme of the process is shown in figure 1.22a. Spalling is extremely simple, versatile, and applicable to a wide range of substrates. It occurs when a tensile-stressed film deposited on a substrate has sufficient stored energy to generate a stress field within the substrate and surpass the substrate's fracture toughness. Once initiated, spalling is nearly instantaneous, thus the entire process, including preparation, handling, and spalling, takes only minutes from start to finish, as compared to the hours required for etching-based ELO techniques [93].

Spalling has been studied for many years as a failure mechanism in civil and structural engineering. However, it was not until the late 1980s that an analytical framework for understanding the mechanics of substrate spalling was clarified [95, 96]. These works opened up the possibility of controlled spalling for use in manufacturing. Only recently, controlled spalling at room temperature has been demonstrated by IBM for different materials including Si (up to 300-mm-diameter wafers), germanium (4" wafers) and GaAs (2" wafers) [94]. In this technique, a stressor layer such as Ni is deposited on the surface of a brittle material by physical vapor deposition sputtering or electroplating and, by manipulating its thickness and stress, it is possible to remove a continuous film at a predetermined depth. A 3J InGaP/InGaAs/Ge solar cell was grown on a Ge substrate and then transferred to a Si substrate using this IBM controlled spalling technology, showing similar characteristics to non-spalled bulk cells, thus indicating that the quality of the epitaxial layers is not compromised as a result of the process [97].

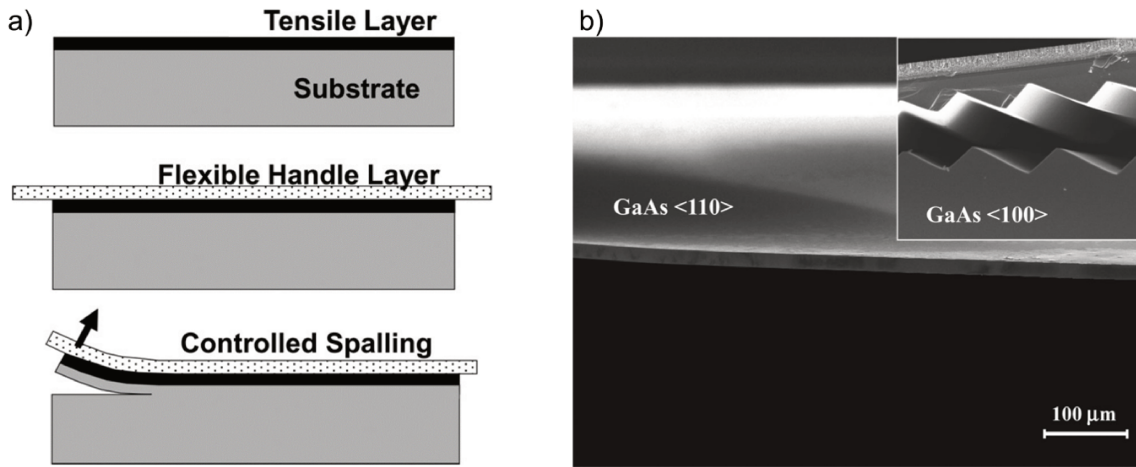


Fig. 1.22 a) Controlled spalling process where first a stress layer is deposited to render the system metastable against spontaneous fracture, a handle layer is then applied and used to propagate surface fracture controllably. b) Cross-section Scanning Electron Microscopy (SEM) image of a $\langle 110 \rangle$ GaAs spalled layer which shows stable fracture parallel to the surface, compared with the unstable fracture in the $\langle 100 \rangle$ orientation (inset) [94].

However, spalling of GaAs substrates in $\langle 100 \rangle$ orientation is difficult due to the polar nature of GaAs bonds. As shown by the inset of figure 1.22b, when the preferred cleavage plane is not oriented in the same plane as where the shear component is minimized, the crack follows the preferred cleavage plane and leads to faceting along two sets of 110 planes. This results in large variations of film depth due to unstable crack propagation and it may introduce defects into the device zone and underlying substrate consuming many microns of material.

1.3.3 Summary

In summary, III-V on Si MJSC have already overcome the Si single-junction efficiency limit and offer the potential of reducing the LCOE by combining the benefits of high-efficient MJSC with the low-cost and abundance of Si. We have seen that despite the extensive research done to improve heteroepitaxy of III-V materials on Si, efficiencies are still limited by high TDD and hence do not exceed the best Si single-junction solar cells. On the other hand, wafer bonding and mechanical stack techniques, which avoid III-V on Si epitaxial growth related problems, achieve today much higher efficiencies and have recently overcome the Shockley-Queisser single-junction efficiency limit of 33%. Table 1.1 summarizes the best III-V on Si solar cells reported to date.

Junction materials	Manufacturing approach	Efficiency (%)	Spectrum	Institution
3J GaInP/GaAs//Si	4T transparent adhesive	35.9 ± 0.5	AM1.5G	EPFL/CSEM/NREL [48]
3J GaInP/GaAs//Si	2T wafer bonded, SAB	33.3 ± 1.2	AM1.5G	Fraunhofer-ISE [79]
3J GaInP/InGaAs/Si	2T metal interconnection	25.5	Xe-lamp	McMaster Univ. [81]
3J GaInP/GaAs/Si	2T epitaxy, GaAsP buffer	19.7 ± 0.7	AM1.5G	Fraunhofer-ISE [69, 34]
2J GaInP//Si	4T transparent adhesive	32.8 ± 0.5	AM1.5G	EPFL/CSEM/NREL [48]
2J AlGaAs/Si	2T epitaxy, AlGaAs buffer	21.2	AM0	Nagoya Institute [57]
2J GaAsP/SiGe	2T epitaxy, SiGe buffer	18.9	ELH-lamp	UNSW Sydney [64]

Table 1.1 Best III-V on Si tandem solar cell efficiencies reported in the literature for the different manufacturing approaches presented.

Highly conductive and transparent bonding interfaces have been demonstrated using the SAB technique. However, direct wafer bonding requires a clean environment, mirror-polished surfaces and ultra-high vacuum conditions. Mechanical stack approach has not these constraints and enables the use of best developed Si bottom cells with front side texturing. Nevertheless, the disadvantages of mechanically stacked solar cells are the optical losses caused by reflection at the interfaces and the shadowing produced by the metallic interconnection grid. In addition, in wafer bonding and mechanical stack approaches substrate reuse is crucial to obtain a competitive LCOE, as III-V expensive substrates are required to independently grow the top cells. ELO is the most mature substrate reuse technique, with small-scale manufacturing operations already underway.

The recent great results, using both wafer bonding and mechanical stack approaches, together with the advancements done in substrate reuse using ELO, predict a promising future for III-V on Si MJSC, which could lead the next generation of high-efficient and low-cost photovoltaics.

1.4 Objectives and outline of the thesis

In this work, 2T 2J AlGaAs//Si and 2T 3J GaInP/AlGaAs//Si solar cells fabricated by wafer bonding are studied, with the main objective of achieving efficiencies over 30%. These choices have been done in accordance to the literature discussed in this report and due to practical reasons. We have chosen the direct wafer bonding approach because of the vast experience and expertise of CEA-LETI in this field and in order to study new wafer bonding techniques. The 2T architecture is the easiest way to interconnect the cells in a module and hence the most widely used configuration. A 2J solar cell could be the best choice for low-cost low-concentration applications because a third junction, with its corresponding tunnel junction, increases costs and complexity.

This dissertation is organized into four chapters. After this introduction on the PV market context, the basic principles of solar cell operation and the motivation for III-V on Si solar cells, **Chapter 2** focuses on wafer bonding. The different wafer bonding techniques reported in the literature are reviewed and the ones performed in this study are discussed in detail, including an innovative approach with promising industrialization potential, opening a new path for III-V on Si processing. Finally, the GaAs//Si bonding interface electrical properties are analyzed using dedicated test devices originally conceived at CEA, allowing to evaluate the interface resistance and the conduction mechanism.

Chapter 3 presents the design and fabrication of the III-V and Si subcells. Optimizations in design and cell processing were carried out thanks to simulations and characterization of device performance, leading to satisfactory results, including record efficiencies. PC1D simulations allowed to identify the key factors that limit the Si subcell performance and possible improvement strategies. Si bottom subcells are fabricated using different thermal diffusion or implantation processes for the emitter formation. Their impact on cell performance is analyzed experimentally by carrier lifetime and quantum efficiency measurements. Finally, the fabrication process after wafer bonding and ARC optimization by transfer-matrix simulation methods are also presented and discussed.

In **Chapter 4**, a new light I - V characterization method, specially adapted for multi-junction solar cells under concentrated light, is developed in order to correctly assess the efficiency of the fabricated III-V on Si tandem cells. First, the challenges and requirements for the accurate MJSC efficiency measurement are reviewed, together with the state-of-the-art of existing characterization methods. Then the measurement principle of the new method is explained, including the manufacturing details of the required pseudo-isotypes. Finally, the validity of the method is demonstrated by measuring 2J and 3J III-V on Si tandem solar cells, obtaining the electrical conversion efficiency.

Finally, in the conclusions, the main results and key findings of this research are presented. Perspectives and future outlooks in order to further improve the performance of III-V on Si tandem solar cells are also discussed.

Chapter 2

Wafer bonding approaches for III-V on Si multi-junction solar cells

A literature review of different wafer bonding techniques for the manufacturing of tandem solar cells is presented in the first section of this chapter. Then the wafer bonding approaches performed in this study are presented, detailing the surface preparation, bonding process and annealing, together with the surface characterization techniques used. Afterwards, the GaAs//Si bonding interfaces morphology and composition are analyzed. In the last section, the interface electrical characterization is performed using 3J solar cells and dedicated test devices, which allow to measure the interface resistance and to assess the conduction mechanisms involved.

2.1 State of the art

As already introduced in section 1.3.2.1, “Direct wafer bonding” refers to the phenomenon that mirror-polished, flat, and clean wafers of almost any material, when brought into contact at room temperature, are locally attracted to each other by weak Van der Waals or hydrogen-bridge forces and spontaneously adhere or “bond” to each other.

To start the bonding and to prevent defects and voids, particle-free and extremely smooth surfaces with Root-Mean-Square (RMS) roughness values below 1 nm are required [98, 99]. In addition, to obtain highly conductive bonding interfaces the native oxides may have to be removed or thinned and the surfaces should be passivated in order to avoid re-oxidation.

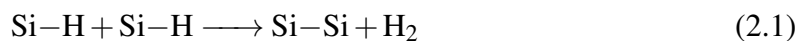
The first step of direct wafer bonding process consists then in preparing the surfaces in order to reduce roughness and eliminate metallic, organic and particle contamination. Consequently, depending on water affinity and the nature of the bonding forces, surfaces can

be classified either as hydrophobic, in which the substrates are bonded by Van Der Waals forces, or hydrophilic, in which the adhesion is assured by hydrogen bonds. Hydrophobic surfaces have little affinity with water and do not get wet easily. Conversely, hydrophilic surfaces have a high affinity for water and hence they get covered with a thin film of adsorbed water as soon as they are in contact with ambient air. The bonding is started by applying a simple pressure to locally expel the air between the two wafers. Then, a wave propagating the bonded area diffuses from the initial point of contact to the whole wafer in a few seconds [100]. Finally, annealing is required to increase the covalent bond density and to consolidate the bonding.

In the next sections, the state of the art of hydrophobic and hydrophilic direct wafer bonding will be presented together with fusion bonding and SAB techniques. Fusion bonding requires continuous pressure and annealing during some hours while in SAB the surfaces are bombarded with an atom beam that removes the native oxide layers, enabling direct formation of covalent bonds without the need of annealing.

2.1.1 Hydrophobic direct wafer bonding

Hydrophobic direct bonding has the advantage of providing semiconductor-to-semiconductor contact without any interfacial layer. This technique is achieved for Si//Si bonding because of the effectiveness of hydrofluoric acid (HF) at rendering oxide-free and electronically passivated surfaces that are stable enough in air to allow further processing [101–106]. HF solution removes the native oxide and forms a mono-atomic hydrogen layer that passivates the surface against oxidation. The attraction forces involved in a hydrophobic bonding are mainly Van der Waals forces (Si-H–H-Si). After annealing, covalent Si-Si bonds are formed at the bonding interface and consolidate the mechanical strength of the assembly according to the following reaction [107]:



Unfortunately, GaAs surfaces suffer from complex native oxides, like Ga₂O₃ [108], that are difficult to eliminate by chemical etching [109]. HF [110, 111] and hydrochloric acid (HCl) [112–116] treatments have been reported in order to remove the GaAs native oxides, resulting in a highly hydrophobic surface, which is temporary passivated by hydrogen or chlorine atoms. However, an extensive exposure to air after the HF dip leads to re-oxidation [117]. GaAs surface passivation through Cl or H bonds is not verified, which limits their stability [118]. In all cases, care has to be taken not to significantly etch the substrate and to preserve a low surface roughness, which can be increased by the deoxidizing treatments.

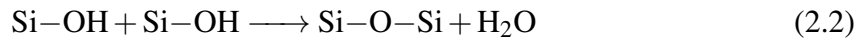
Even though some wafer bonding realizations using a GaAs hydrophobic surface have been reported [110, 119, 114–116], a GaAs//Si interface showing ohmic behavior has not been yet reported.

2.1.2 Hydrophilic direct wafer bonding

Si hydrophilic surfaces consist of an oxide layer to which water molecules are attached via intermediate OH-groups. Hydrogen-bridge forces are then established in this case between the two substrates [120]. Hydrophilic surfaces are easier to prepare because of the native oxide naturally formed in Si and GaAs when they are in contact with air. However, if the oxides are not thin enough, conduction through the interface can be reduced, which hampers its use for tandem solar cells.

Si//Si hydrophilic direct wafer bonding has been extensively studied at CEA-LETI [121–126]. The wafers are covered by native SiO₂ films that have hydrophilic properties due to the presence of silanol groups (Si–OH) that form hydrogen bonds with water. In ambient air and room-temperature, a few mono-layers of water are then adsorbed and trapped at the bonding interface, figure 2.1a.

Annealing at $T < 150^\circ\text{C}$ increases bonding interface electronic density [122], which is associated with the closure of the interface, as illustrated in figure 2.1b, and is driven by the formation of siloxane (Si–O–Si) covalent bonds between the wafers at the contact points [107] through the following reaction:



This process does not evolve to a complete closure of the interface because of the trapped water. Annealing at $T > 150^\circ\text{C}$ decreases bonding interface electronic density [122] due to water diffusion through the native oxide, figure 2.1c, which then oxidizes the Si bulk and increases the thickness of the native oxide interlayer through reaction 2.3. The hydrogen formed this way is mainly trapped at the bonding interface in gas form and becomes a source of bonding discontinuities in the form of bubbles.



GaAs//Si hydrophilic bonding presents similar problems concerning the low conductivity of the interface and the trapped water which causes H₂ bubbles [127]. CEA and Fraunhofer-ISE collaboration team manufactured GaAs on Si solar cells by hydrophilic direct wafer bonding but using the Si substrate only as a handler and not in an active multi-junction

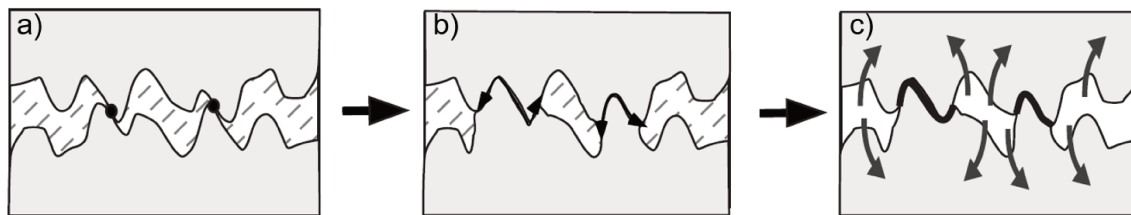


Fig. 2.1 a) $\text{SiO}_2/\text{SiO}_2$ interface before annealing in which water is trapped. b) Contact point extension driven by reaction 2.2 during annealing at $T < 150^\circ\text{C}$. c) Water diffusion through the oxide leading eventually to Si bulk oxidation and production of hydrogen through reaction 2.3 when annealing at $T > 150^\circ\text{C}$ [122].

configuration because of the bad conductivity of the GaAs//Si interface [128]. As will be explained in section 2.2, different bonding techniques have been studied in this work in order to overcome these issues.

2.1.3 Fusion bonding

Fusion bonding is not spontaneous, requiring high pressures and annealing during hours due to the high roughness or contamination of the surfaces. Highly conductive and transparent GaAs//Si hetero-structures were realized by a Tokyo university team [129] using this technique. Si and GaAs pieces of 1 cm^2 were deoxidized by wet-chemical etching, brought in contact at room temperature and annealed at 300°C for 3 hours under a pressure of 100 KPa in the presence of air. Ohmic behavior was achieved for p-GaAs//p-Si and p-GaAs//n-Si junctions using highly doped GaAs and Si surfaces with concentrations over 10^{19} cm^{-3} . The $\sim 2\text{ nm}$ thickness of the amorphous layer that was formed at the interface was sufficiently thin to provide ohmic interfacial conductivity by inducing tunneling current. However, bonding of Si and GaAs at high temperatures has the disadvantage of thermal stress building up during cool down, which can lead to the formation of cracks. In addition, trapped water at the interface, which may be able to escape in the case of 1 cm^2 small pieces, is probably another issue that prevents defect free bonding of full wafers using this technique.

Another possibility is the use of transparent conductive oxide (TCO) as the bonding interlayer. NREL presented a method for bonding of III-V materials to Si using a transparent conductive indium zinc oxide interlayer with interface resistivity below $1\ \Omega\text{cm}^2$ for 1.2 cm^2 cleaved samples [130]. Bonding was performed under vacuum, at temperatures ranging from 100 to 350°C , for 2 hours under a pressure of 22.5 KPa. The TCO layer is smooth and provides optical transmission as well as electrical conduction. This particular structure could

be easily applied to tandem solar cells on Si and in particular on heterojunction with intrinsic thin-layer (HIT) Si cells [131], which already incorporate a TCO at the top surface.

2.1.4 Surface activated bonding

In SAB technique the surfaces are bombarded in ultra-high vacuum with an atom or ion beam, as shown in figure 2.2. This removes the native oxide superficial layers via sputtering and creates dangling bonds that enable direct formation of covalent bonds at room temperature without the need of annealing. This is a great advantage because high temperatures can degrade cell performance or even produce cracks due to the difference of thermal expansion coefficient between GaAs and Si. However, sputtering results in the formation of a few nanometers thick amorphous interlayer that could degrade electrical performance.

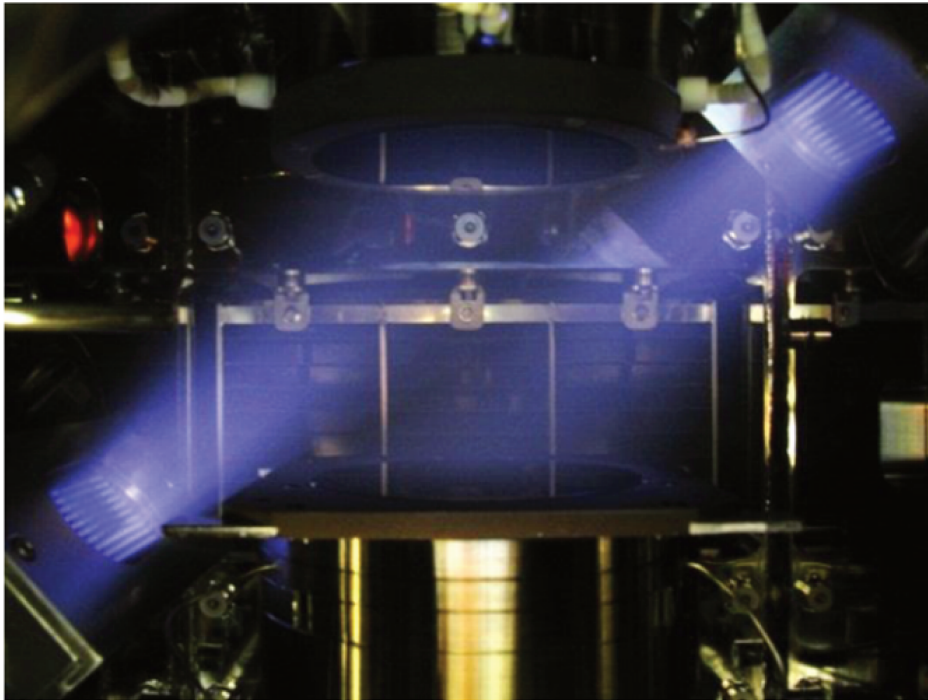


Fig. 2.2 Photo of a SAB vacuum chamber with an Ar fast atom beam irradiating both GaAs and Si surfaces [132].

Tokyo University team demonstrated Si//Si bonding at room temperature using SAB [133] and then GaAs//Si hetero-interfaces were realized [134, 135]. The amorphous interlayer was shown to be reduced from 11.5 to 2.0 nm after annealing at 600 °C with a corresponding improvement of the I – V behavior [136]. However, this high temperature can degrade the layer structure by diffusion of dopants and an ohmic interface was not yet achieved.

Osaka University team has also studied the SAB technique [137–139] and in collaboration with Sharp they manufactured a 2T 3J GaInP/GaAs//Si solar cells of 2 mm^2 [140] in which the bonding p-GaAs//n-Si interface served as the tunnel junction between the middle and bottom subcells. After annealing at $395\text{ }^\circ\text{C}$ for 1 min, the 3 nm amorphous interlayer seems to recrystallize and the interface resistance was estimated to $70\text{ m}\Omega\text{cm}^2$.

Fraunhofer-ISE team has obtained the lowest GaAs//Si interface resistance to date and the best solar cell results using the SAB technique. Ar and He Fast Atom Beams (FAB) were studied [141] at different acceleration voltages [142]. A highly conductive and transparent interface between n-GaAs//n-Si isotype hetero-junction was demonstrated with a resistance of only $3.6\text{ m}\Omega\text{cm}^2$ using Ar FAB surface preparation [143]. Immediately after the FAB, the wafers were brought into contact at $120\text{ }^\circ\text{C}$ and a force of 10 kN was applied for 5 min. Then annealing for 1 min at $395\text{ }^\circ\text{C}$ needed to form the contacts, increased strongly the interface conductivity thanks to the thickness reduction of the amorphous damaged layer and due to recovery of defects caused by the FAB, leading to lower carrier trapping. Transmission Electron Microscopy (TEM) image, shown in figure 2.3a, revealed a $\sim 5\text{ nm}$ thin amorphous interlayer formed by the Ar FAB treatment before bonding [144].

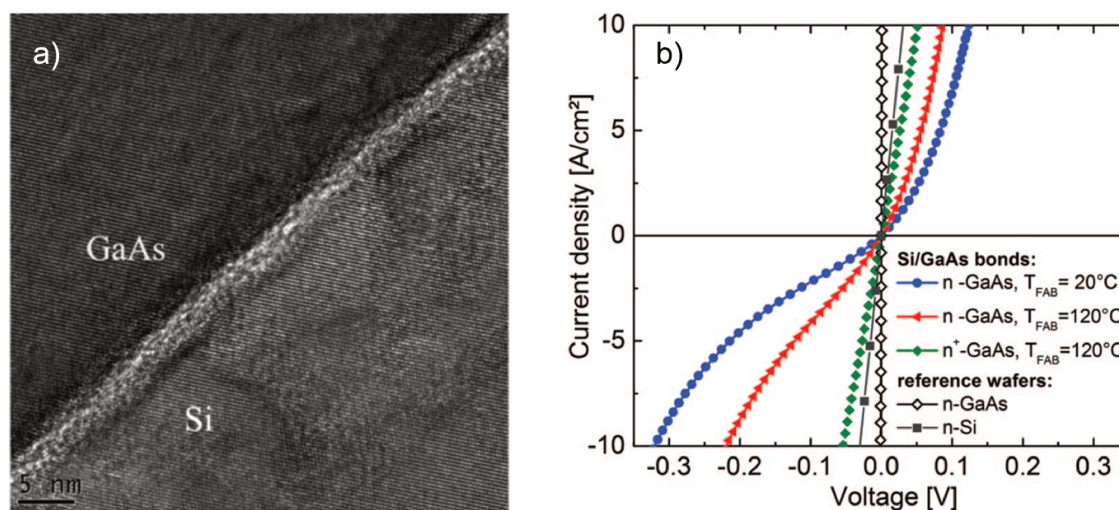


Fig. 2.3 a) Transmission Electron Microscopy (TEM) image of the GaAs//Si interface obtained with SAB resulting in a $\sim 5\text{ nm}$ amorphous interlayer produced by the atom bombardment [144]. b) I - V characteristics of different n-Si/n-GaAs SAB interfaces after annealing (1 min at $395\text{ }^\circ\text{C}$). Wafers were exposed to the FAB at a temperature T_{FAB} of $20\text{ }^\circ\text{C}$ or $120\text{ }^\circ\text{C}$ and had different n-GaAs doping levels ($n = (1.3 \pm 0.3) \times 10^{18}\text{ cm}^{-3}$, $n^+ = (9.4 \pm 0.7) \times 10^{18}\text{ cm}^{-3}$). I - V characteristics of single n-GaAs and n-Si wafers with metal contacts are plotted as a reference [143].

In this case, the tunnel junction was placed on the GaAs wafer and therefore its operation is independent from the n-GaAs//n-Si interface. High electron concentrations n were needed in both GaAs and Si surfaces in order to obtain ohmic I - V curves, shown in figure 2.3b. For this reason, a highly doped n^+ -GaAs bonding layer was grown on the GaAs substrate with $n_{\text{GaAs}} = (9.4 \pm 0.7) \times 10^{18} \text{ cm}^{-3}$ and was bonded to the Si wafer, which had a surface concentration of $n_{\text{Si}} = (4.0 \pm 0.5) \times 10^{20} \text{ cm}^{-3}$. The higher electron density reduces the potential barrier and width of the space charge region at the bonding interface and therefore promotes the transport of thermally activated carriers through thermionic emission conduction. The thinner space charge region might also enable quantum tunneling through the barrier. Using this optimized SAB technique, Fraunhofer-ISE has demonstrated the best 2T 3J solar cell using a Si bottom subcell (GaInP/GaAs//Si), with a record conversion efficiency of 33.3% under one sun [145, 146, 79].

A Korean team [147] has developed a similar bonding technique to create ohmic GaAs//Si interfaces. In this case, GaAs and Si wafers (with doping concentrations of 10^{19} cm^{-3}) are first dipped in NH_4OH and HF respectively to remove the native oxides and then the two surfaces are treated by Ar plasma using a reactive ion etching chamber to activate the surfaces. This process could reduce the complexity and equipment cost compared to the classic SAB. The two wafers are then directly bonded in the presence of air by applying a light pressure. No voids were observed at the interface and only a $\sim 1.5 \text{ nm}$ thick interfacial amorphous layer was formed. Interface resistance was found to be $8.8 \text{ m}\Omega\text{cm}^2$ without applying any thermal annealing after the bonding process.

2.1.5 Summary

Table 2.1 summarizes the advantages and open challenges for the different bonding techniques reported in the literature. Hydrophobic direct wafer bonding works good for Si//Si but GaAs oxides are difficult to eliminate and surfaces re-oxidize due to ineffective passivation. Hydrophilic surfaces are instead easy to prepare, but the oxide interlayer and the water trapped at the interface, that produces bonding defects, reduce interfacial conductivity. Ohmic behavior has been obtained for GaAs//Si interfaces fabricated by fusion bonding technique, however only small areas were reported and it requires annealing during hours at high pressure. Best electrical results are obtained using SAB, thanks to the oxide free interfaces. Nonetheless, this technique requires ion bombardment in ultra-high vacuum, which adds complexity and cost.

Bonding	Advantages	Challenges
Hydrophobic	no oxide interlayer for Si//Si	difficult to eliminate GaAs oxides and to passivate the GaAs surface
Hydrophilic	easy to prepare the surfaces	oxide interlayer water trapped at the interface produces H ₂ bubbles
Fusion	GaAs//Si ohmic behavior reported	requires annealing during hours and high pressure only reported for small surfaces
SAB	covalent bonds without annealing no oxide interlayers best reported electrical results	requires ion bombardment and ultra-high vacuum formation of an amorphous layer

Table 2.1 Advantages and challenges of the different III-V on Si bonding techniques reported in the literature.

2.2 Wafer bonding approaches performed

Different wafer bonding techniques are studied in this work as an alternative to the known SAB technique. The objective is to find a new bonding process, resulting in equally suitable GaAs//Si hetero-structures with low defectivity and interface resistance, but without the need of ultra-high vacuum and surface ion bombardment. This is of crucial importance in order to reduce costs and enable an easy industrialization of III-V on Si solar cells by wafer bonding.

Hydrophilic wafer bonding was investigated due to the extensive experience of CEA in this topic and due to the difficulties found in the preparation of hydrophobic GaAs surfaces [118]. GaAs//Si hydrophilic wafer bonding was performed using two different surface treatments. In one case (GaAs//Si native), the Si surface is left oxidize under room temperature, forming a native oxide layer. On the other case (GaAs//Si UV-O₃), an UV-O₃ oxidizing treatment is applied to the Si surface. A novel approach was also implemented, consisting in growing a GaAs epitaxial layer on the Si substrate in order to perform a GaAs//GaAs hydrophilic wafer bonding. All these wafer bonding approaches are compared to the SAB technique by analyzing the chemical composition, morphology and electrical properties of the bonding interfaces.

2.2.1 Surface preparation

Prior to bonding, the surface defectivity and roughness of both GaAs and Si 100 mm substrates are characterized. Defect mapping is done by ultraviolet (UV) illumination using

KLA-Tencor Surfscan 6200 automatic equipment based on the scattering of light produced by defects and particles of different sizes. Even if the bonding process is done inside a cleanroom (ISO 6 standard), there are still particles that are deposited at the wafer surfaces and therefore a cleaning treatment has to be applied.

The wafer surface roughness is characterized by Atomic Force Microscopy (AFM), which is based on the interaction between the wafer surface and the tip of a cantilever, whose deflection is measured using a diode laser and a photodetector. If the roughness is too high (RMS over 0.5 nm using a $1\ \mu\text{m}^2$ scan) a CMP treatment has to be applied.

Organic contamination on Si wafers, mainly produced by hydrocarbons of the form CH_x , is removed by Caro's acid (H_2SO_5), which is an aqueous solution of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) that allows to decompose the organic molecules without degrading the substrates [148]. However, it produces additional particle contamination and hence the surfaces are further cleaned with SC1 and SC2 solutions (SC for Standard Cleaning). SC1, an aqueous solution composed of ammonia (NH_4OH) and H_2O_2 , removes the native oxide containing the particles and replaces it by a particle-free oxide. SC2 is an aqueous solution of HCl and H_2O_2 which allows to remove metallic contamination. This sequence was developed within the Radio Corporation of America from which it comes its common name RCA [149]. Figure 2.4, obtained with a Surfscan equipment, shows an example of the defects detected before and after these cleaning treatments.

CMP is then applied in order to reduce surface roughness. The CMP process uses an abrasive and corrosive colloidal silica slurry, composed of SiO_2 particles and liquid bleach (NaClO), in conjunction with a polishing pad. The rotating pad is pressed against the wafer removing material and producing a smooth surface. Finally, the slurry residues are removed using a brush scrub with an NH_4OH solution. Figure 2.5, obtained by AFM, shows the surface roughness before and after the CMP.

In the case of hydrophilic GaAs//Si UV- O_3 bonding, an UV- O_3 oxidizing treatment is applied to the Si surface. An UV light lamp irradiating at 185 and 254 nm is used. 185-nm UV light dissociates molecular oxygen (O_2) into triplet atomic oxygen, $\text{O}(^3\text{P})$. $\text{O}(^3\text{P})$ combines then with O_2 and generates ozone (O_3). On the other hand, 254-nm UV light dissociates O_3 , forming O_2 and singlet atomic oxygen, $\text{O}(^1\text{D})$. $\text{O}(^1\text{D})$ has strong oxidation power, which breaks down surface contaminants into volatile compounds and reacts with the Si substrate producing a controlled oxide layer. For hydrophilic GaAs//Si native bonding, the Si wafers are left oxidize at room temperature and a native oxide is formed instead.

The SiO_2 native and UV- O_3 oxides are analyzed by Fourier-Transform Infrared Spectroscopy (FTIR) and compared to thermally grown oxide. This analytical technique probes

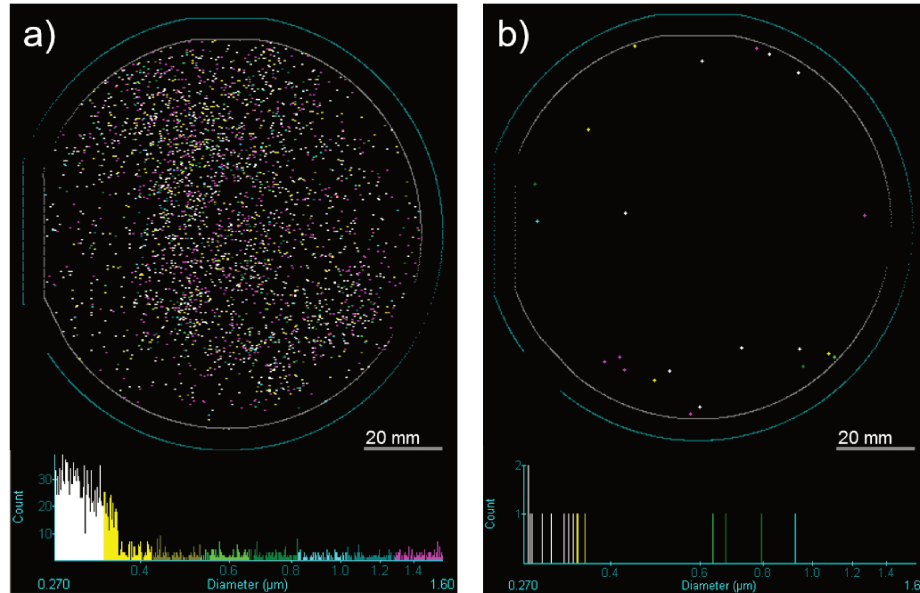


Fig. 2.4 Wafer defect mapping using Surfscan, a) before and b) after Caro+RCA surface cleaning treatments. The defect counting and classification by diameter is included. In this example the defects are reduced from 3491 to only 22 after the cleaning.

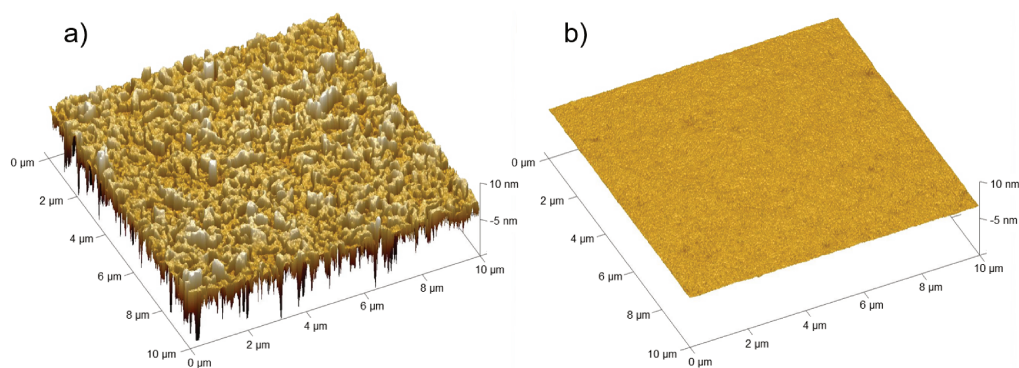


Fig. 2.5 Surface roughness 3D contours obtained by AFM, a) before and b) after CMP. In this example RMS roughness is reduced from 3.5 nm to only 0.2 nm.

the vibrational properties of a material, providing insights into the microscopic structure. In figure 2.6, the longitudinal optical peak at around 1256 cm^{-1} is shown for the different oxide layers. This peak is related to stretching motion of Si-O bonds. As can be seen, the UV-O₃ peak is shifted in relation to the native oxide and it is very close to the thermal oxide peak, suggesting that the UV-O₃ oxide is denser than the native oxide [150, 151].

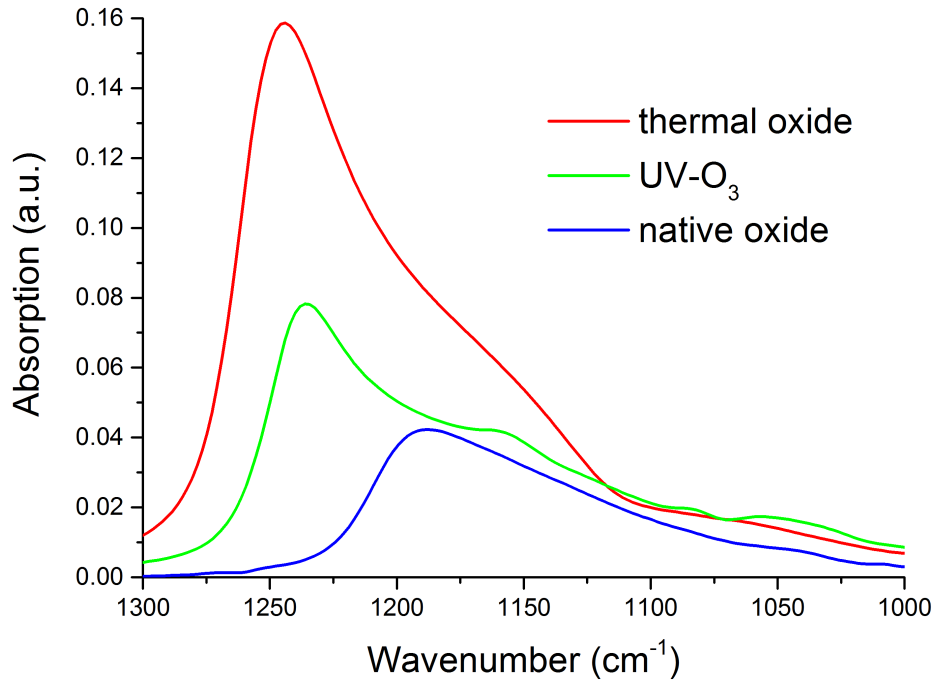


Fig. 2.6 FTIR analysis of the SiO₂ oxide layer formed by UV-O₃ treatment compared to the native oxide and thermally grown oxide.

For GaAs//Si SAB, both Si and GaAs surfaces are bombarded just before bonding by an Ar ion beam with an energy of around 200 eV, removing this way the native oxide layers by sputtering and leaving a very reactive surface with dangling bonds.

For epi-GaAs//GaAs hydrophilic bonding, the Si surface preparation differs from the others. In this case, a Siconi[®] treatment [152] is applied in the first place in order to remove the native oxide and passivate the surface. Siconi is a remote plasma assisted dry etch process that simultaneously exposes the substrate to NF₃ and NH₃. SiO₂ is then transformed into a salt which is sublimated by applying a low temperature annealing. Afterwards, a 200 nm thick n-type GaAs epitaxial layer with a doping concentration of 10^{19} cm^{-3} is grown by MOVPE and then the same surface treatments applied to the GaAs wafers are also performed. Table 2.2 summarizes the different surface treatments applied to the Si wafers for every bonding technique.

In all cases, for GaAs wafers the surface preparation starts with the CMP. Then, an HF solution is applied followed by an ammonium sulfide $(\text{NH}_4)_2\text{S}$ treatment. Sulfide surface passivation has been reported to improve the electrical properties by removing oxygen and thus reducing the surface trap state densities [115, 106]. Finally, a scrub using NH_4OH solution is also applied in order to remove the particle contamination just before the bonding or the next surface treatment. GaAs surfaces are then left oxidize under room temperature forming a native oxide layer.

Bonding method	Si surface treatment
GaAs//Si native	Caro, RCA, CMP, NH_4OH scrub
GaAs//Si UV- O_3	Caro, RCA, CMP, NH_4OH scrub, UV- O_3
GaAs//Si SAB	Caro, RCA, CMP, NH_4OH scrub, Ar ion beam
epi-GaAs//GaAs	SiCONi, epi-GaAs, CMP, HF, $(\text{NH}_4)_2\text{S}$, NH_4OH scrub

Table 2.2 Different surface treatments applied to the Si wafers for every bonding technique performed.

2.2.2 Bonding process and annealing

GaAs//Si or epi-GaAs//GaAs hydrophilic wafer bonding is performed at room temperature under vacuum. The bonding energy provided at this stage by the hydrogen bonds is weak and the bonding is reversible. Therefore, a thermal treatment is applied under N_2 atmosphere for 1 hour in order to increase bonding strength and covalent bond density. However, due to the difference of thermal expansion coefficient between GaAs and Si, high temperatures can induce material defects or even cracks that make the bonding structure unstable. At first, the annealing temperature was limited to 100 or 200 °C because higher temperatures caused cracks and the samples broke. In the case of III-V on Si MJSC fabrication, the GaAs substrate is removed by wet chemical etching after the bonding, leaving the few-micrometers-thick III-V top active layers on the Si bottom subcell. Therefore, at this stage a 300 °C annealing could be performed with reduced stored elastic energy compared with the bulk/bulk structures.

For GaAs//Si SAB, GaAs and Si wafers are loaded into an EVG580 ComBond® ultra-high vacuum chamber [153]. As already explained, the oxide layers formed on GaAs and Si wafer surfaces are then removed by an Ar beam with an energy of around 200 eV. This creates a very reactive surface with dangling bonds and therefore, when the surfaces are brought into

contact under ultra-high vacuum, covalent bonds are formed at room-temperature without the need of annealing.

2.2.3 Interface characterization

After bonding and annealing, the bonding interface morphology is characterized by cross-sectional High Resolution Transmission Electron Microscopy (HRTEM). In this technique, a beam of electrons is transmitted through the sample and an image is formed thanks to the interaction of the electrons with the atoms of the material as the beam is transmitted. Very high resolution can be obtained, allowing to resolve individual atoms and the crystallographic structure.

In hydrophilic bonding, oxide is found at the interface with a thickness of 4 nm for GaAs//Si native, figure 2.7a, 2 nm for GaAs//Si UV-O₃, figure 2.7b and less than 1 nm for epi-GaAs//GaAs, figure 2.7c. This is in accordance with the native oxides formed at the surfaces and the UV-O₃ oxidizing treatment applied. The thicker oxide found for GaAs//Si native bonding suggests that the water trapped at the interface is able to diffuse through the native oxide and react with Si forming additional SiO₂ and H₂, following equation 2.3 as already explained in section 2.1.2. Conversely, for GaAs//Si UV-O₃ the thinner oxide may suggest that water does not react as much with Si. This could be explained by the denser oxide produced by the UV-O₃ treatment, that prevents water from diffusing out of the interface.

Energy-Dispersive X-ray spectroscopy (EDX), a technique consisting in focusing a beam of electrons into the sample in order to stimulate a characteristic X-ray emission from which the chemical composition can be obtained, revealed the presence of sulfur at the interface due to the (NH₄)₂S treatment applied to the GaAs wafers. In the case of GaAs//Si SAB, shown in figure 2.7d, argon is found at the interface instead of oxygen, which is also in accordance with the Ar FAB that removes the native oxides [154]. However, a 3 nm amorphous layer is formed due to the high energy with which the Ar ions bombard the surface producing sputter-induced displacement damage [155].

In figure 2.8, the GaAs epilayer directly grown on Si for the epi-GaAs//GaAs bonding is shown. This layer presents high number of defects and threading dislocations due to the lattice parameter mismatch between GaAs and Si. Nonetheless, no defects are found in the active III-V layers that are independently grown on the GaAs wafer, showing the great advantage of wafer bonding.

Interface defectivity is characterized by Scanning Acoustic Microscopy (SAM). This technique is based on the analysis of acoustic wave propagation through different media with

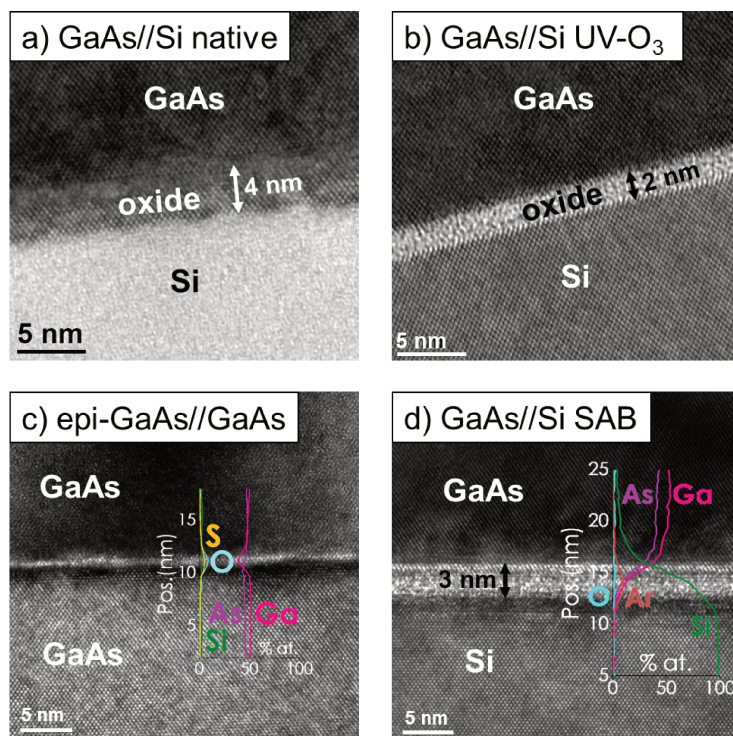


Fig. 2.7 HRTEM images of the interfaces obtained for every different bonding technique, together with the EDX profiles: a) GaAs//Si native, b) GaAs//Si UV-O₃, c) epi-GaAs//GaAs and d) GaAs//Si SAB.

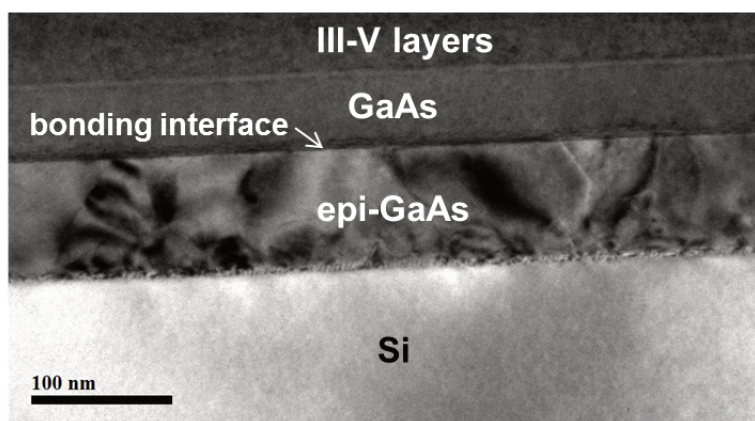


Fig. 2.8 TEM image of the epi-GaAs//GaAs bonding showing a high number of defects and threading dislocations in the GaAs epilayer directly grown on Si.

a characteristic impedance, which allows to detect bonding defects and voids at the interface [156].

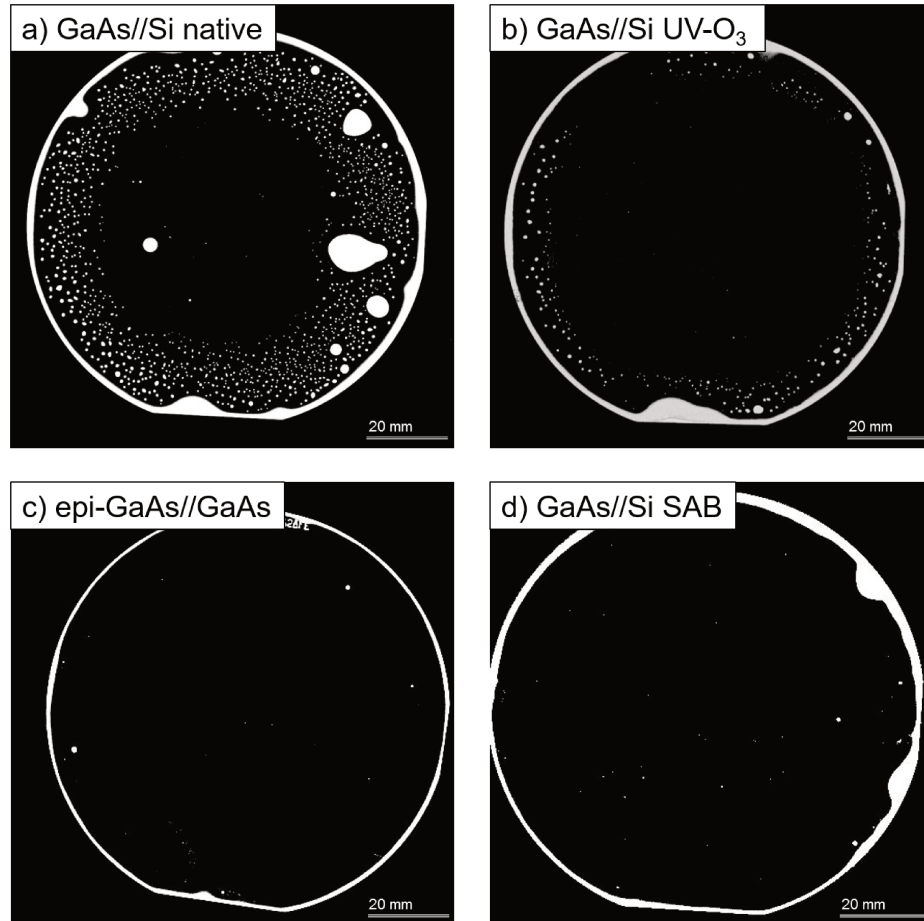


Fig. 2.9 SAM images of the bonding interfaces obtained for every different bonding technique: a) GaAs//Si native, b) GaAs//Si UV-O₃, c) epi-GaAs//GaAs and d) GaAs//Si SAB. White areas represent regions where the bonding has not been successful.

The SAM image of the GaAs//Si native bonding interface is shown in figure 2.9a. White areas represent regions where the bonding has not been successful. These defects and cavities may be caused by particle contamination or due to water trapped at the interface. The higher interface defectivity, compared to GaAs//Si UV-O₃ shown in figure 2.9b, is in agreement with the also thicker oxide revealed by HRTEM, figure 2.7. This suggests that the main cause of these defects is water, which as already explained reacts with Si, following equation 2.3, forming additional SiO₂ and releasing bubbles of H₂. For GaAs//Si UV-O₃, the lower defectivity could be explained by a temperature shift in H₂ production due to the denser oxide, allowing the bonding interface to become stronger with the increment in

temperature and thus capable of storing the H_2 produced later at higher pressure without causing additional defects.

Interestingly, epi-GaAs//GaAs hydrophilic bonding, shown in figure 2.9c, present a high quality interface with very few defects. The interface obtained by GaAs//Si SAB, figure 2.9d, is also near defect-free, in accordance with the lack of water and oxides at this interface.

In summary, four bonding approaches have been performed, describing the surface preparation and bonding process. The resulting interfaces have been characterized by analyzing the chemical composition and morphology. The results obtained are summarized in table 2.3.

Bonding method	Interface composition by TEM	Bonding defectivity by SAM
GaAs//Si native	oxide of 4 nm	high
GaAs//Si UV-O ₃	denser oxide of 2 nm	low
epi-GaAs//GaAs	oxide of 1 nm	low
GaAs//Si SAB	Ar + amorphous layer of 3 nm	low

Table 2.3 Summary of the results obtained by TEM and SAM.

In the next section, the electrical characterization of the bonding interfaces will be discussed.

2.3 Electrical characterization

Electrical characterization is important in order to asses the interface resistance, R_{int} . Since R_{int} is added to the total series resistance of the solar cell, its electric properties have to be optimized so that the power losses by Joule heating are negligible compared to the photo-generated power. The maximum resistance allowed for a solar cell is therefore a function of the photocurrent at one sun, J_L^* , and light concentration factor, X , as shown in the following equation [157, 158].

$$R_{S \text{ max}} \approx \frac{V_T}{X J_L^*} \quad (2.4)$$

where V_T is the thermal voltage. For this study we take a low concentration of around 10 suns and an expected photo-current of about 10 mA/cm^2 , resulting in $R_{S \text{ max}} \approx 300 \text{ m}\Omega\text{cm}^2$.

To predict the electrical properties of the GaAs//Si heterojunction, the energy band diagram at the interface is considered. For the ideal case of a defect-free interface, this depends essentially on the material-specific electron affinities, the band gap energies of the

semiconductors and their surface charge carrier concentrations [159]. The electron affinity rule, or Anderson's rule [160], is then applied and therefore bringing into contact GaAs and Si semiconductors of respective affinities $\chi_{\text{GaAs}} = 4.07 \text{ eV}$ [161] and $\chi_{\text{Si}} = 4.01 \text{ eV}$ [162] results in a discontinuity of the conduction bands [163], as shown in figure 2.10. An equilibrium is established between the electrons flowing from the material of the weakest work function (Si) to that of the higher work function (GaAs) and vice versa for the holes, resulting in the same Fermi energy level in both semiconductors. A negative space charge region appears then on the GaAs side while a positive space charge region is present on the Si side, forming a staggered gap heterojunction [159] with a barrier of height $q\Phi_b$. However, if the semiconductor surfaces are doped till degeneration, with high surface doping concentrations so that the Fermi level energy is higher than barrier, carriers can then easily pass over the interface resulting in a low R_{int} and an ohmic behavior.

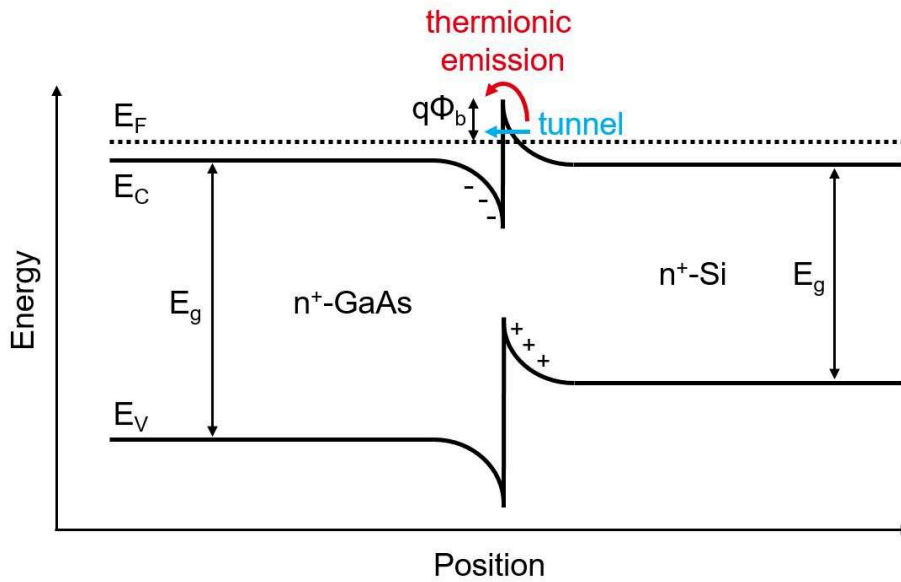


Fig. 2.10 Schematic energy-band diagram of a bonded n^+ -GaAs/ n^+ -Si heterojunction. Thermionic emission and quantum tunnelling conduction mechanisms to overcome a potential barrier $q\Phi_b$ are illustrated.

In real heterojunctions the interface electrical properties can be degraded because of the presence of defects, dislocations or contamination [164]. In n-doped semiconductors, acceptor-like defect levels may exist at the bonding interface trapping electrons and creating this way additional charges that increase even more the potential barrier. In addition, non-conducting surface oxides increase both the height and length of the barrier. If the barrier is smaller than V_T , the thermal energy of charge carriers is sufficient to overcome it and then the transport across the bonding interface can be described in this case with the thermionic

emission model. On the other hand, if the barrier is thin enough, quantum mechanical tunneling through the barrier is also possible. In both cases, diode-like non-ohmic I – V curves may result. In contrast to thermionic emission, quantum tunneling process is almost temperature-independent and only relevant for very thin potential barriers [165].

The electrical characterization of the different GaAs//Si bonding interfaces have been done using both a dedicated test structure and actual 3J GaInP/AlGaAs//Si solar cells. The advantages of dedicated test devices are the simplified fabrication process and the direct access to R_{int} , although it could be different since their surface doping is not exactly the same as for the tandem cells.

2.3.1 Light I – V measurements of 3J solar cells

In the case of 3J GaInP/AlGaAs//Si solar cells, the III-V top subcells and the Si bottom subcell are manufactured separately before bonding. Solar cell fabrication process, design and optimization will be discussed thoroughly in chapter 3. The top GaInP and middle AlGaAs subcells are grown inverted on the GaAs substrate and an n^+ -type bonding layer is added with a doping concentration over $5 \times 10^{18} \text{ cm}^{-3}$. The Si bottom subcell is fabricated from a p-type wafer by diffusion process in order to form an n^+ -type emitter and a p^+ -type Back Surface Field (BSF), resulting in a Si front surface doping concentration after CMP of around 10^{20} cm^{-3} . For epi-GaAs//GaAs bonding, an n^+ -type GaAs epilayer with a doping concentration of 10^{19} cm^{-3} is grown on the Si surface as described previously.

After bonding, the cells are processed, removing the GaAs substrate and forming the metal contacts, which requires a short annealing of 1 min at 395 °C. Schemes of the final structures fabricated by GaAs//Si or epi-GaAs//GaAs bonding techniques are depicted in figure 2.11.

The light I – V curves of the 3J devices fabricated with different bonding techniques were first measured using a SpectraNova solar simulator under 1-sun, as shown in figure 2.12. This is a standard single-source solar simulator and therefore, as will be explained in chapter 4, it is not well adapted for the characterization of series connected MJSC because it can produce a very high uncertainty in the current measurement due to spectral mismatch. Fill factor can be also impacted to a lesser extent by spectral mismatch, but for the study presented in this chapter it can give a good qualitative estimation of the bonding interface conductivity.

The devices fabricated by GaAs//Si native and UV- O_3 hydrophilic bonding techniques present distorted I – V curves with a very pronounced “S-kink” close to V_{OC} . This can be explained by a too high built-in potential barrier for majority charge carriers formed at the

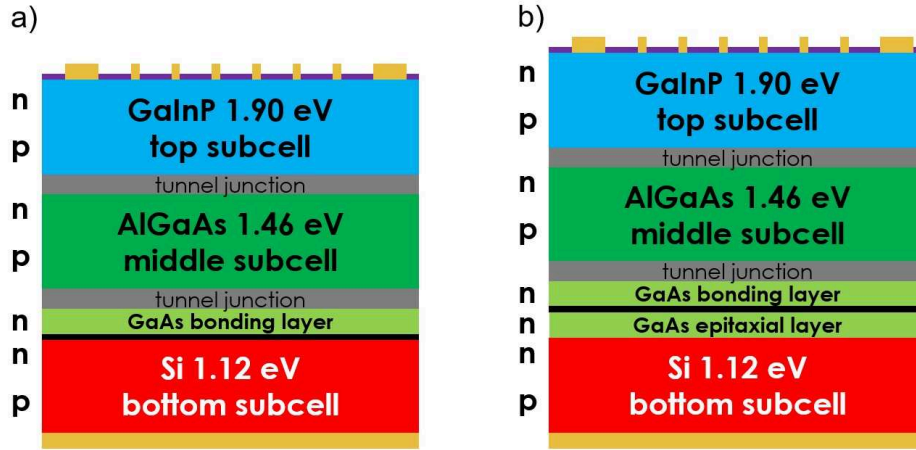


Fig. 2.11 Scheme of the 3J solar cell structures fabricated by a) GaAs//Si SAB and hydrophilic bonding and b) epi-GaAs//GaAs hydrophilic bonding. The black line represents the bonding interface.

GaAs//Si interface [127, 166]. Conversely, the I – V curve of the SAB-bonded devices does not show any distortion, in accordance with other SAB solar cells previously reported in literature [146, 167], suggesting that the “S-kink” most probable cause is the oxide interlayers that are removed in the case of SAB.

Interestingly, although devices fabricated by epi-GaAs//GaAs hydrophilic bonding technique also present an “S-kink” distortion, they exhibit superior performance compared to GaAs//Si bonded devices, with a high fill factor of 80%, which is relatively close to that of SAB at 87%. This is in agreement with the thinner oxide revealed by HRTEM in figure 2.7c and with the lower interface defectivity detected by SAM analysis in figure 2.9c, confirming the high potential of this novel bonding approach.

The impact of the different bonding techniques on the 3J solar cell FF has been studied in this section, which gives qualitative information about the conductivity of the interface. However, it is difficult to extract R_{int} using this complex structures. For this reason, dedicated test devices are considered in the next section.

2.3.2 Test devices for interface resistance characterization

In order to directly measure R_{int} , dedicated test devices were manufactured. The test devices used in this study are an adaptation of an original structure conceived at CEA-LETI [168], allowing to directly measure the I – V characteristic of a thin interface in the middle of a thick stack.

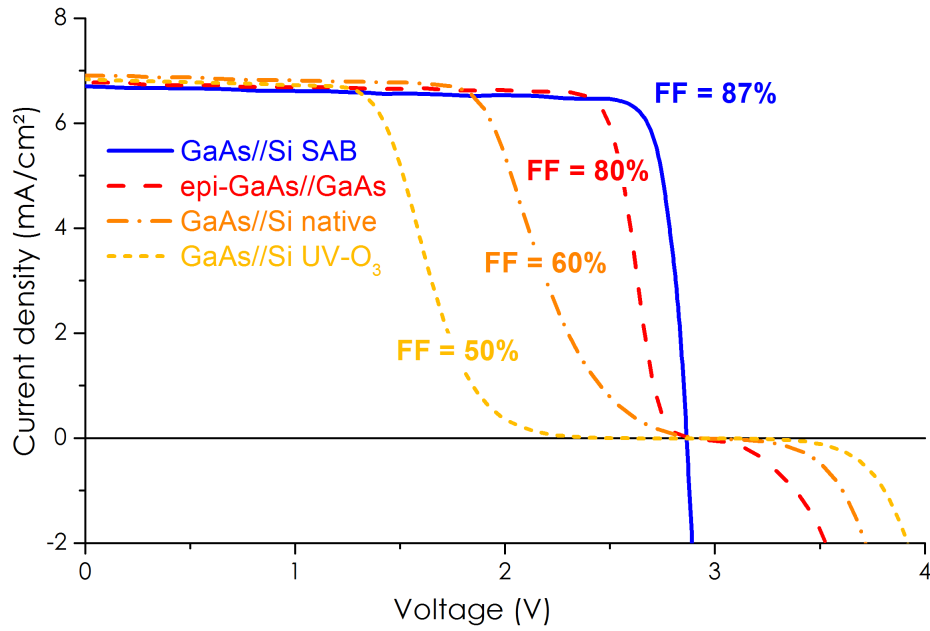


Fig. 2.12 I - V curves of 3J solar cells fabricated by the different bonding techniques with the corresponding fill factors. GaAs//Si hydrophilic bonded devices present a pronounced “S-kink” distortion, while for epi-GaAs//GaAs technique this effect is limited and SAB devices are not affected.

As shown in figure 2.13, trenches to isolate the area of interest are performed by saw-cut. One of the cuts stops just above the interface, leaving a margin of around $25\ \mu\text{m}$, and the other just below at the same distance. Terminal T3 is used to apply a voltage and T4 is connected to the mass, forcing this way a transverse current through the stack parallel to the cutting lines. Since no current flows through the lateral contacts, the potential difference measured using terminals T1 and T2 is only due to R_{int} . This allows the direct measurement of R_{int} without the contributions of the substrates and metal/semiconductor contact resistances. Concerning the device dimensions, the width of the saw-cut is $100\ \mu\text{m}$, that of the two lateral contacts is $250\ \mu\text{m}$ and the surface of the central block is $0.25\ \text{cm}^2$.

A 2-dimension numerical simulation using Technology Computer Aided Design (TCAD) is useful to demonstrate the interest of this device. The structure was simulated using Silvaco Atlas software for an injected current of $I = 0.1\ \text{A}$, as shown in figure 2.14. The quasi-parallel potential lines, represented in white, validate the measurement principle: T1 and T2 give access to the direct measurement of the potential drop between the top of the interface (point 1 in the figure in orange) and the bottom (point 2 in blue). The equipotential curvature on the edges of Si is due to diffusion of current from a reduced area (center block) to the entire width of the device, but this does not influence the measurement [118].

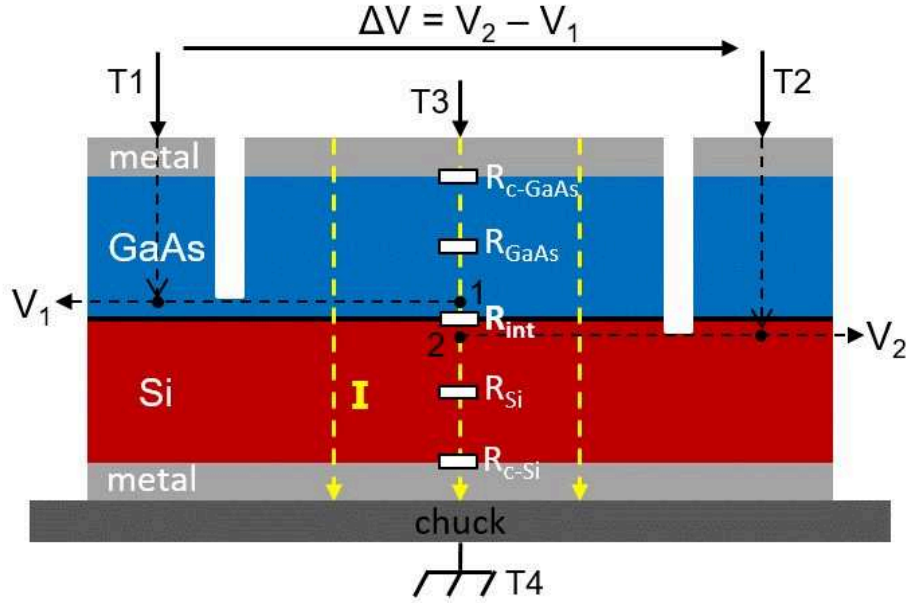


Fig. 2.13 Scheme of the saw-cut 4-terminal test device. The current flows vertically from T3 to T4, while the potential drop due to R_{int} is measured using the lateral plots T1 and T2, thus allowing the direct measurement of R_{int} .

2.3.2.1 Fabrication process

The 100 mm wafers used for the fabrication of the test devices are similar as the ones used for the fabrication of the solar cells. However, in this case there are no p-n junctions with an n-type emitter on top of the p-type base. Therefore, instead of p-type Si wafers, n-type doping is chosen in order to perform the same n-GaAs//n-Si bonding. The Si and GaAs wafer thicknesses are 525 and 475 μm respectively, with doping concentrations around $n_{\text{Si}} = 2 \times 10^{19} \text{ cm}^{-3}$ and $n_{\text{GaAs}} = 10^{18} \text{ cm}^{-3}$. These doping concentrations are lower than the ones obtained in the solar cell bonding surfaces due to the absence of n^+ -type emitter on the Si wafer (doping concentration after CMP of around 10^{20} cm^{-3}) and highly doped n^+ bonding layer on the GaAs wafer (doping concentration of $5 \times 10^{18} \text{ cm}^{-3}$).

As shown in figure 2.15a, the first step on the fabrication process of these devices is the bonding of the two wafers. This was done by SAB and epi-GaAs//GaAs bonding techniques, since they had shown the most promising characteristics. After the bonding, metal contacts are formed by sputtering of Ti/Pt/Au on the Si side and evaporation of Ni/Ge/Au/Ti/Au on the GaAs side, followed by metal annealing during 1 min at 395 $^{\circ}\text{C}$, figure 2.15b. Afterwards, a saw is used to perform the cuts just above and below the interface and to isolate the different devices. This is a critical point, because metal contamination on the sides of the interface could create a short circuit. Therefore, in the first place, a small cut of around 50 μm deep

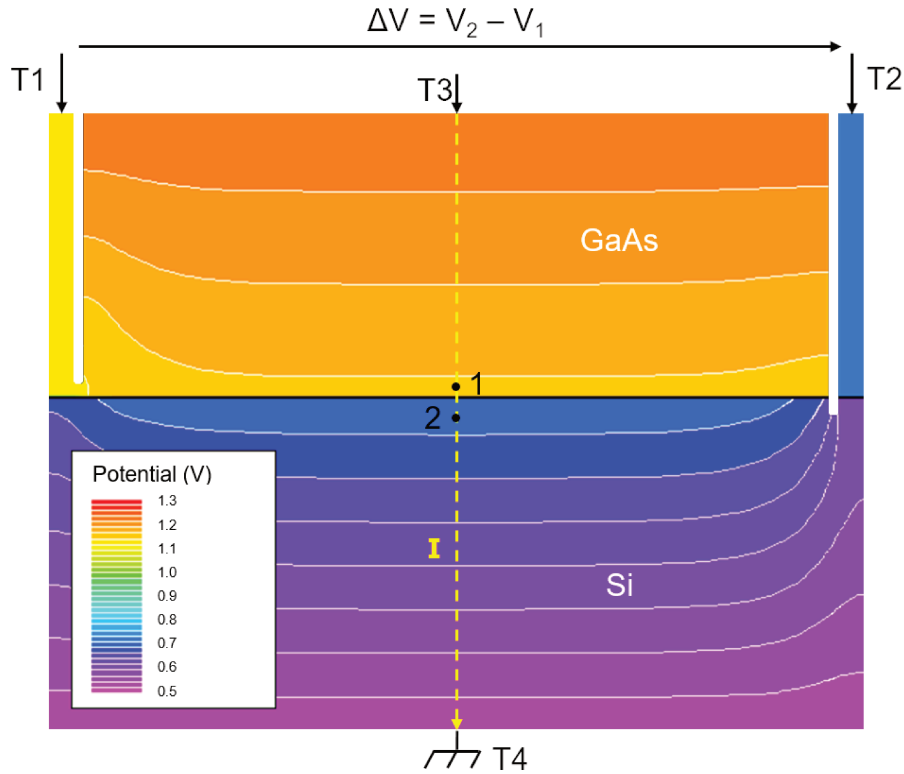


Fig. 2.14 Simulated saw-cut test device structure using Silvaco Atlas TCAD for an injected current of $I = 0.1$ A, equipotentials are represented by white lines.

is performed using a $150\text{ }\mu\text{m}$ wide saw just to remove the metal, figure 2.15c, followed by a high pressure water cleaning to take away the metal residues. Then, a second cut with a more precise $100\text{ }\mu\text{m}$ wide saw is performed in the previously defined metal-free sections, figure 2.15d. High precision is required during this step in order for the cuts to be just above and below the interface due to the small margin of error of only $25\text{ }\mu\text{m}$. The good execution of the saw cuts is confirmed by microscope inspection, as shown in figure 2.16.

2.3.2.2 I - V measurements

In order to determine the relevance of the saw-cut test devices, two types of I - V measurements are compared with each other: the already explained 4-terminal measurement (saw-cut 4T) shown in figure 2.13 and a standard 2-terminal (2T) transverse measurement, which does not require the precise saw cuts just above and below the interface but includes the substrate resistances together with metal/semiconductor, metal/chuck and metal/probe contact resistances.

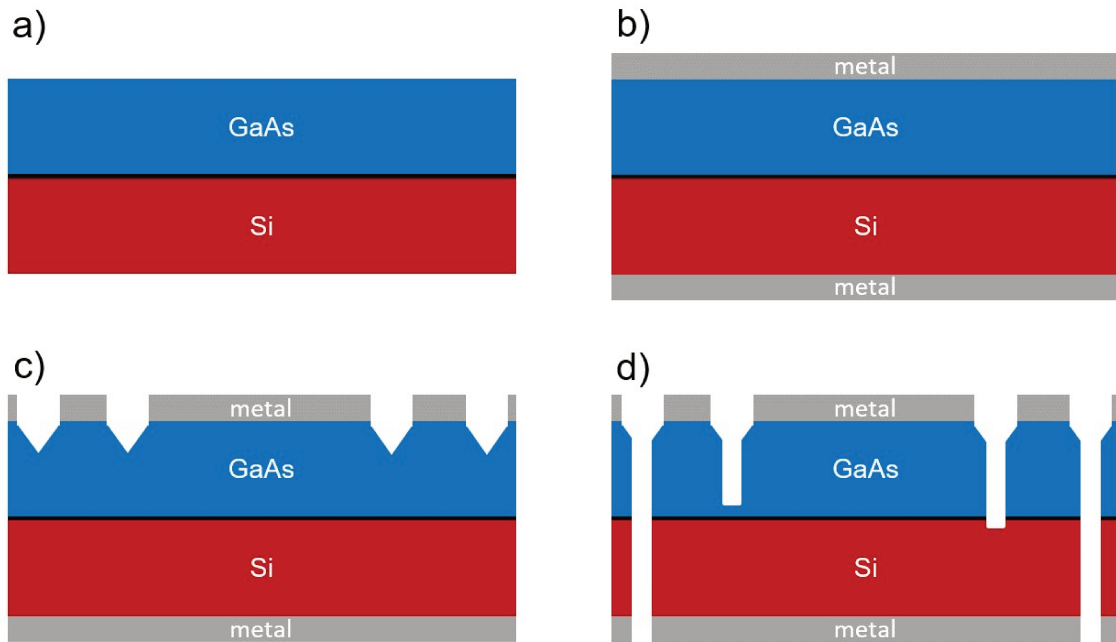


Fig. 2.15 Fabrication process of the saw-cut test devices: a) wafer bonding, b) metallization, c) large saw-cut to remove metal and high pressure water cleaning, d) thinner and more precise saw-cut just above and below the bonding interface and to isolate the different devices.

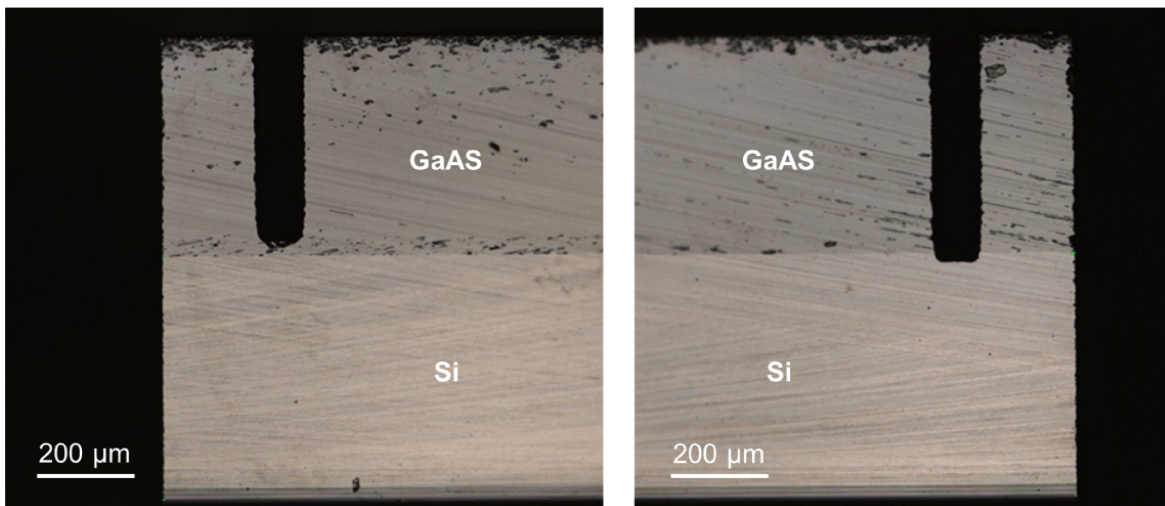


Fig. 2.16 Optical microscope images of the saw cuts stopping a) just above (30 μm) and b) just below (20 μm) of the bonding interface.

The I - V characteristics of test devices fabricated either by SAB or hydrophilic epi-GaAs//GaAs bonding and measured using a 2T or saw-cut 4T configuration are shown in figure 2.17. For epi-GaAs//GaAs bonding, the I - V curves are non-linear with a diode like characteristic due to the Ga_2O_3 insulating oxide layers, as already reported for GaAs//GaAs bonding in the literature [114, 169, 170]. The two different regimes observed could be explained as follows. At high voltages, when $|V| \geq \Phi_b$, the carriers can pass over the interface potential barrier. The current is then limited by the series resistances of the rest of the device and the regime is ohmic with $J = 1/R_s(V - \Phi_b)$. At low voltages, when $|V| < \Phi_b$, the potential barrier cannot be overcome and the current does not flow. SAB interfaces on the other hand present a linear ohmic behavior thanks to the oxide-free interface.

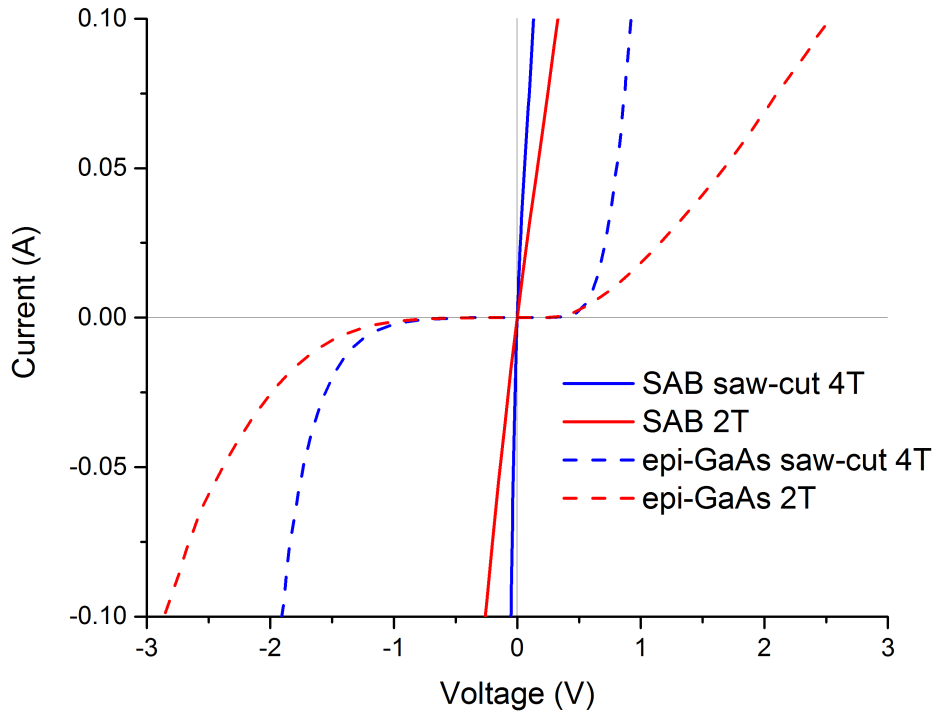


Fig. 2.17 I - V characteristics of test devices fabricated either by SAB or hydrophilic epi-GaAs//GaAs bonding and measured using 2T or saw-cut 4T configuration.

At low polarization ($V \sim 0$) the current is directly influenced by the interface potential barrier and therefore R_{int} can be calculated by the following equation:

$$R_{\text{int}} = \left(\frac{\partial V}{\partial J} \right)_{V=0} \quad (2.5)$$

Table 2.4 summarizes the surface resistances obtained by multiplying R_{int} by the interface area. As expected, the 4T configuration gives a lower resistance because it directly measures

R_{int} without including the other series resistances of the device and probes. This technique is therefore much more precise in order to characterize the interface electrical properties.

Bonding technique	Measurement configuration	Resistance at $V = 0$ ($\text{m}\Omega\text{cm}^2$)
SAB	saw-cut 4T	210
SAB	2T	750
epi-GaAs//GaAs	saw-cut 4T	∞
epi-GaAs//GaAs	2T	∞

Table 2.4 Surface resistances of the different test devices for 2T and saw-cut 4T configurations, calculated by multiplying R_{int} from equation 2.5 by the interface area.

The interface resistance of the SAB bonding device is found to be $210 \text{ m}\Omega\text{cm}^2$, which is lower but close to the $300 \text{ m}\Omega\text{cm}^2$ limit that was estimated for our solar cells using equation 2.4. However, it has to be noted that the surface doping concentration for the test devices is lower than for the solar cells. This can have a significant influence on the interface conductivity, because increasing the surface doping concentration increases the Fermi energy level and thus the barrier height is lowered. In addition, this reduces the space charge region length, resulting in a thinner barrier that can be passed by quantum tunneling besides thermionic emission conduction. Even so, the measured R_{int} using the test devices can be interpreted as an upper limit for the solar cells, allowing to conclude that the interface resistance does not limit the performance of the tandem cells fabricated by SAB.

Nonetheless, in order to know precisely the actual R_{int} of the solar cells, new test devices are being fabricated including an n^+ -type diffusion in the Si surface and an n^+ bonding layer on the GaAs wafer in order to have the same surface doping concentrations as for the solar cells. This could not be included in this work because the fabrication is still ongoing.

2.3.2.3 I – V measurements as a function of temperature

Temperature-dependent I – V characteristics were measured for the SAB test devices in order to study the transport mechanism through the bonding interface. As shown in figure 2.18, the conductivity of the samples decreases significantly with decreasing temperature, with ohmic behavior at 300 K and diode-like I – V curves at lower temperatures.

Non-ohmic behavior can be explained by the formation of a potential barrier at the interface, caused by electron trapping in ion beam induced defects, thereby generating a negative interface charge [143]. The strong temperature dependence indicates that the carriers

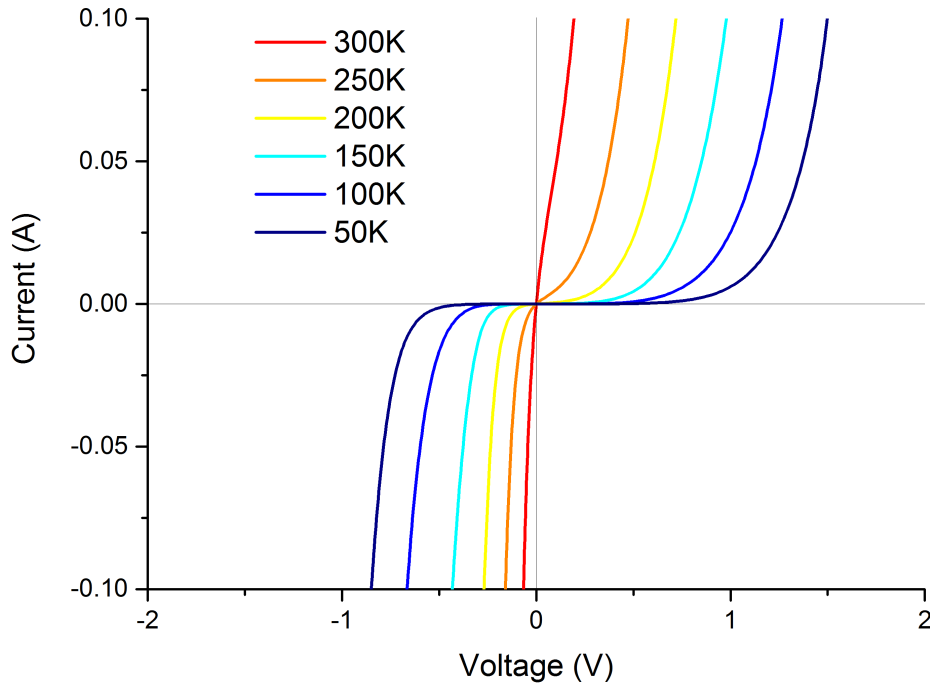


Fig. 2.18 I – V characteristics of test devices fabricated by SAB and measured using the saw-cut 4T configuration versus temperature.

overcome the potential barrier mainly by their thermal energy, as already reported in the literature [143]. The conduction mechanism is then described by the thermionic emission model and not by quantum tunneling, which is almost independent of temperature [165].

2.4 Conclusions

Different bonding approaches have been evaluated for the fabrication of III-V on Si solar cells: hydrophilic GaAs//Si bonding with native oxides, hydrophilic GaAs//Si bonding with UV-O₃ oxidizing treatment, hydrophilic GaAs//GaAs bonding by growing a GaAs epitaxial layer on Si and GaAs//Si SAB. Near defect free interfaces, characterized by SAM, are obtained for hydrophilic wafer bonding using UV-O₃ and by epi-GaAs//GaAs wafer bonding approach. However, the oxides formed at the bonding interface degrade the electrical conductivity resulting in diode-like I – V curves. Nonetheless, despite this non-ideal behavior, 3J solar cells fabricated with this novel technique present FF values as high as 80%, showing a great potential and opening a new path for III-V on Si integration. Best electrical results are obtained by SAB, despite the amorphous interlayer formed at the interface, as already reported in the literature. For this reason, SAB technique was the preferred bonding approach to conduct the subcell design optimization presented in the next chapter. Even so, epi-

GaAs//GaAs approach has the advantages of not requiring ultra-high vacuum and ion beam surface treatments, which can be major impediments for an easy industrialization.

Original test devices conceived at CEA have been fabricated and adapted for the study of the GaAs//Si bonding interface. Even if the surface doping of these structures is not the same as for the tandem solar cells, R_{int} evaluated this way can be interpreted as an upper limit, allowing to conclude that the interface resistance does not limit the performance of the tandem cells fabricated by SAB. Measurements as a function of temperature have also revealed the presence of a potential barrier for SAB bonding due to Ar FAB induced defects. At room temperature, thermal energy is enough to overcome this barrier producing an ohmic behavior. However, the conductivity decreases at lower temperatures showing diode-like I – V curves. This dependence on temperature suggests that the conduction mechanism through the interface can be described by the thermionic emission model.

Chapter 3

Design and fabrication of III-V on Si multi-junction solar cells

In this chapter, the design and fabrication of the III-V and Si subcells is presented. Optimizations in the design and fabrication process were carried out thanks to simulations and characterization of device performance, leading to satisfactory results, including record efficiencies. The first part is dedicated to the top subcell design for the 2J tandem cell. The choice of the materials is discussed together with thickness reduction of the GaAs bonding layer.

In the second part, the Si bottom subcell design is studied, specially for the 3J GaInP/AlGaAs//Si cell, since in this case, current mismatching between the III-V and Si bottom subcells is high. PC1D simulations are performed, allowing to identify the key factors that limit the Si subcell performance and possible improvement strategies. Si bottom subcells are fabricated with CZ and FZ substrates using different thermal diffusion or implantation processes for the emitter and BSF formation. Their impact on cell performance is analyzed experimentally by carrier lifetime and quantum efficiency measurements. Finally, the fabrication process after wafer bonding and ARC optimization by transfer-matrix simulation methods are also presented and discussed.

3.1 Design and fabrication of III-V top subcells

The GaInP top and AlGaAs middle subcells of the 3J cell were fabricated and designed at Fraunhofer-ISE as reported in reference [144]. Conversely, the top subcell of the 2J cell was designed and optimized at CEA and the epitaxy was carried out by one of our partners, either the III-V Lab or IQE. The III-V epitaxial layers of wafer bonded III-V on Si solar cells are

grown inverted (i.e. starting from the top of the cell) on a GaAs substrate by MOVPE. In MOVPE, ultra pure gases are combined into a reactor at elevated temperatures, causing a chemical interaction between the metalorganic precursor molecules containing the required elements and the wafer surface, resulting in the deposition of epitaxial layers on the substrate.

3.1.1 III-V subcell structure

The III-V subcells are composed of four layers: a window layer on the top, the emitter, the base and a Back Surface Field (BSF) on the back. Tunnel junctions are grown in between of the subcells to connect them in series [171]. The general structure of the n-on-p 2J tandem solar cell studied in this work is presented in figure 3.1, along with a scheme of the energy band diagram in equilibrium.

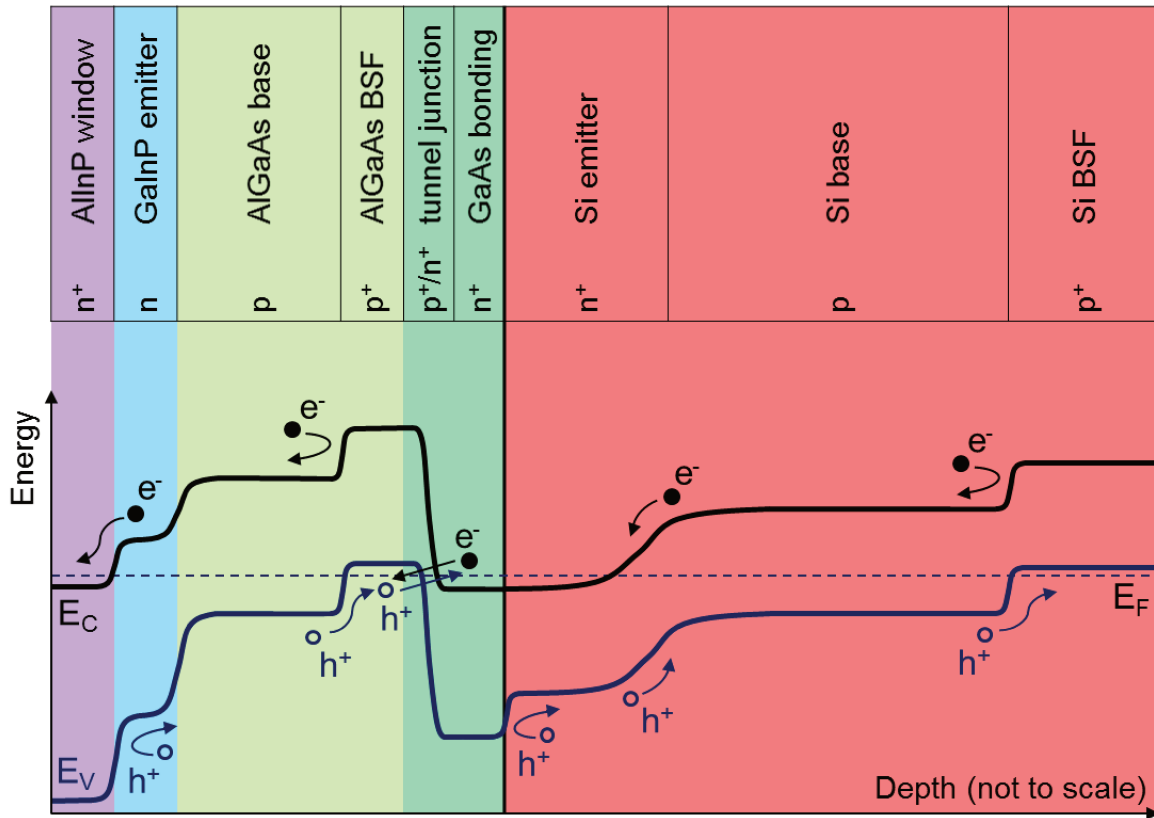


Fig. 3.1 2J n-on-p tandem solar cell structure studied in this work along with the energy band diagram in equilibrium. The window principle forming a barrier for holes (h⁺) and a sink for electrons (e⁻) is illustrated, while the BSF has the opposite purpose. In the thin tunnel junction, electrons photo-generated in the bottom subcell recombine with the top subcell holes.

The **window layer** is used to passivate the emitter, reducing its surface recombination. Thanks to its high doping and wide bandgap, it forms a barrier for the minority charge carriers (holes in this case) photo-generated in the emitter, preventing this way its diffusion and recombination in the front surface, while becoming a sink for majority carriers (electrons) that are collected in the metal contacts. The window should absorb as little light as possible, since the photo-generated carriers in this layer are most likely recombined in the front surface. Therefore, a wide bandgap material and a very thin layer are required.

Prior to the window, a highly doped contact or **cap** layer, not shown in figure 3.1, is grown to ensure the ohmic behavior of the front metal contact. As this layer can absorb light, it has to be removed from the active regions, remaining only below the metal contacts.

The most energetic photons are absorbed in the **emitter**. This layer must be thin enough to allow collection of the photo-generated carriers before they recombine. However, since majority carriers (electrons) flow also laterally in this layer before they are collected by the metal grid fingers, a sufficient thickness is required in order to reduce power losses due to sheet resistance. For this same reason, high doping is also convenient since it increases conductivity, although this can also reduce minority carrier lifetime and hence collection due to creation of defects [172].

In the **base**, lower energy photons are absorbed and collected. It must be thick enough to absorb most of the low energy photons and therefore, minority carrier lifetime must be high enough to allow carrier collection. High doping increases V_{OC} by reducing equilibrium minority carrier concentration and thus recombination. However, there is a trade-off because it can also promote recombination due to creation of defects that reduce lifetime.

The **BSF** is used to passivate the base surface in the same way as the window for the emitter. Therefore, it must also be highly doped to form a potential barrier for minority carriers (electrons) generated in the base and become a sink for majority carriers (holes). Wide bandgap and thin layer are also convenient to allow transmission of the light not absorbed in the base to the next subcells.

Tunnel junctions are n-p diodes which function is to connect in series the different subcells. As shown in figure 3.1, the electrons photo-generated at the bottom subcell recombine in the tunnel junction with the holes produced at the top subcell. Therefore, the electrons that are actually collected at the front metal contacts and pass through the external circuit are only the ones produced at the top subcell. The tunnel junctions must be very thin and heavily doped, thereby resulting in filled electron states on the n-type layer aligning with empty hole states on the p-type layer, separated only by a very thin barrier, so that electrons can pass through by quantum tunneling and recombine with the holes. The recombination in

the tunnel junctions prevents the actual detrimental recombination of photo-generated carriers in each of the subcells. Although this may be counter-intuitive, the key is to remember that MJSC principle is to increase voltage and not total current, resulting in higher voltages but lower currents than single-junctions. Tunnel junction materials should have wide bandgaps in order to allow light transmission to the subcells underneath. However, tunnel current decreases exponentially with the increase in bandgap energy, which hinders the realization of low resistance wide-bandgap tunnel junctions [173].

A highly doped **bonding layer** is needed in the case of wafer bonded III-V on Si solar cells to allow ohmic conduction through the III-V//Si interface, as already explained in chapter 2. In addition, as shown in figure 3.1, the n-type GaAs bonding layer could also act as a window layer for the Si subcell, reflecting hole minority carriers [49]. However, the defects produced at the III-V//Si interface during the bonding process may prevent an effective surface passivation. A bandgap as large, at least, as the upper subcell and a thin layer are recommended in order to allow transmission of low energy photons to the bottom subcells. Bonding layers made of wide-bandgap materials are then favorable, but III-V on Si bonding procedures are usually only adapted for GaAs. In this case, a trade-off may exist with high doping since it can cause band-gap narrowing and thus absorb more light [174].

3.1.2 Top subcell design and optimization for a 2J tandem cell

The design of the top subcell for the 2J cell is the result of an extensive literature review followed by an optimization methodology consisting of measuring in the first place the External Quantum Efficiency (EQE) and Reflectance (R), as a function of light wavelength, λ . These characterization techniques, further explained in appendix A, allow to assess the photon absorption, reflection and photo-generated carrier collection efficiency for every different photon wavelength. These data combined with simulations are used to quantify the loss mechanisms due to recombination and reflection, enabling the optimization of the different subcell layers and ARC.

From the EQE , the subcell photo-generated currents, I_L , can be estimated using equation A.3, which can be used as a figure of merit to drive the optimization procedure. The Internal Quantum Efficiency (IQE), calculated using equation A.1, takes into account only the photons absorbed and not the ones reflected and therefore it is a measure of the recombination losses. In addition, the Current-Matching ratio (CM) between the subcells can be calculated following equation A.4, which is an essential parameter in the performance of series-connected MJSC.

3.1.2.1 Choice of materials

The starting point for the 2J top subcell design is the choice of the materials for every layer. As seen in figure 1.17, $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ has a direct bandgap of 1.7 eV, which is optimum for the 2J top subcell. The increase of Al content leads to a significant rise of E_g with very little variation of lattice constant [175], enabling to grow this material lattice matched to the GaAs substrate without the introduction of strain and defects in the lattice, resulting in low interface recombination [176]. With $x > 0.6$, $\text{Al}_x\text{Ga}_{1-x}\text{As}$ bandgap becomes indirect with values around 2.1 eV and thus can be used as the window or BSF layers [177]. However, the main problem of Al-based compounds is their sensitivity to oxygen. In contact with air the surface oxidizes and any trace of O_2 or H_2O in the vapor phase during epitaxy will lead to oxygen incorporation in the epitaxial layers, creating deep level traps, which act as recombination centers lowering minority carrier lifetime [178, 179]. Residual oxygen may come from contaminated sources as well as from the reactor chamber environment as a result of small leakages in the system [59]. In the case of a p-on-n structure, a high interface recombination velocity has been reported between p-type AlGaAs window and p-type GaInP emitter [180] due to a high conduction band offset [179].

$\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ lattice matched to GaAs is less sensitive to oxygen due to the absence of Al [179]. However, the direct bandgap of this material varies between 1.9 to 1.8 eV as a function of sub-lattice ordering [181]. In addition, its absorption is higher than for $\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$ due to the lower and direct bandgap [176], which is detrimental for its use as a window layer.

$\text{Al}_{0.5}\text{In}_{0.5}\text{P}$ is also lattice matched to GaAs and it has a high indirect bandgap of 2.3 eV [182]. n-type AlInP has lower reactivity with oxygen than AlGaAs [183] and low interface recombination with GaInP [180]. However, p-type AlInP is especially sensitive to oxygen, it is difficult to dope it above 10^{17} cm^{-3} and in addition a high potential barrier forms at the interfaces with the p-GaAs cap layer and with the p-GaInP emitter in p-on-n GaInP solar cells [184, 185]. Table 3.1 summarizes the advantages and disadvantages of the different window layer materials.

Initially, only solar cells with a p-on-n structure could be grown and thus an AlInP window for a GaInP top subcell was not a possible option due to the problems related with p-type AlInP. In addition, the GaInP bandgap is higher than the optimum 1.7 eV for a series connected 2J top subcell, so GaInP is in principle not the best material for the base. For the first iterations, the emitter and base were then made of $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ and the window and BSF with $\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$. Because of the possible oxidation in the presence of air, a 10 nm thick GaInP layer was grown on top in order to prevent the contact with air, forming a 2-layer window. This top subcell structure for the 2J cell, presented in table 3.2, will be referred as

Material	Advantages	Disadvantages
$\text{Al}_x\text{Ga}_{1-x}\text{As}$	E_g varies with Al content small variation in lattice constant low recombination with GaAs	high Al reactivity with O_2 recombination due to O_2 deep traps p-AlGaAs/p-GaInP recombination
$\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$	free of Al, insensitive to O_2 low recombination with GaAs	lower and direct bandgap higher absorption E_g varies with ordering
$\text{Al}_{0.5}\text{In}_{0.5}\text{P}$	lower Al reactivity with O_2 higher indirect E_g , less absorption low recombination with GaInP	contains Al barrier at interfaces for p-type high doping not possible for p-type

Table 3.1 Summary of window layer materials advantages and disadvantages.

structure “2J-A”. 2J tandem cells with almost identical structure but opposite doping type, i.e. in a n-on-p configuration, were also realized and will be referred also as 2J-A structure.

Layer	Material	Bandgap (eV)	Doping (cm^{-3})	Thickness (nm)
cap	GaAs	1.4	$p^+ = 5 \times 10^{18}$	100
window	$\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$	1.9	$p^+ = 2 \times 10^{18}$	10
window	$\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$	2.1	$p^+ = 2 \times 10^{18}$	20
emitter	$\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$	1.7	$p^+ = 2 \times 10^{18}$	100
base	$\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$	1.7	$n = 10^{17}$	2000
BSF	$\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$	2.1	$n^+ = 2 \times 10^{18}$	150
tunnel junction	GaAs	1.4	n^+	25
tunnel junction	GaAs	1.4	p^+	25
bonding	GaAs	1.4	$p^+ = 5 \times 10^{18}$	500

Table 3.2 2J-A top subcell structure with p-on-n configuration. Tunnel junction details are confidential.

For the next solar cell designs and fabrication iterations, an n-on-p structure was chosen in order to use an n-AlInP window. This requires the emitter to be made of GaInP in order to have low interface recombination, which is also advantageous because it does not contain Al. Nonetheless, its 1.9 eV bandgap is higher than the optimum for a 2J cell and for this reason, the base was made of $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$, allowing to keep the top cell bandgap at 1.7 eV. An n-GaInP/p-AlGaAs heterojunction is formed this way, as first suggested in 1994 in order to reduce recombination in the highly doped GaAs emitter of common GaAs single-junction

Layer	Material	Bandgap (eV)	Doping (cm ⁻³)	Thickness (nm)
cap	GaAs	1.4	$n^+ = 5 \times 10^{18}$	200
window	Al _{0.5} In _{0.5} P	2.3	$n^+ = 2 \times 10^{18}$	25
emitter	Ga _{0.5} In _{0.5} P	1.9	$n^+ = 2 \times 10^{18}$	100
base	Al _{0.2} Ga _{0.8} As	1.7	$p = 10^{17}$	2000
BSF	Al _{0.6} Ga _{0.4} As	2.1	$p^+ = 2 \times 10^{18}$	150
tunnel junction	AlGaAs		p^+	25
tunnel junction	GaAs	1.4	n^+	25
bonding	GaAs	1.4	$n^+ = 5 \times 10^{18}$	100

Table 3.3 2J-B top subcell structure with n-on-p configuration. Tunnel junction details are confidential.

solar cells [186]. This top subcell structure for the 2J cell, presented in table 3.3, will be referred as structure “2J-B”.

The *IQE* of different 2J top subcells with 2J-A and 2J-B structures are shown in figure 3.2a. Top subcells with 2J-A structure have lower collection for short wavelengths, from 300 to 500 nm, compared to subcells with 2J-B structure and to the GaInP top subcell of the 3J. As these short wavelengths are absorbed in the first layers, this suggests high recombination losses in the window and emitter. As shown in figure 3.2b, the Ga_{0.5}In_{0.5}P/Al_{0.6}Ga_{0.4}As (10 nm/20 nm) 2-layer window absorbs indeed more light than the one made of Al_{0.5}In_{0.5}P, which explains in part the lower performance of subcells with 2J-A structure. In addition, the highly doped Al_{0.2}Ga_{0.8}As emitter may suffer from low minority carrier lifetime due to doping induced defects and deep level traps related to O₂ contamination. Subcells with 2J-B structure have *IQE* values at short wavelengths similar to those obtained for the Al-free GaInP 3J top subcell designed by Fraunhofer-ISE and are even higher from 500 nm on, showing the good design and quality of these cells. I_L calculated with equation A.3, increased by 7.3% with respect to the 2J-A structure, thanks to the short wavelength improved performance.

3.1.2.2 GaAs bonding layer and tunnel junction

For the 2J cell, the tunnel junction and bonding layers made of GaAs, with a smaller bandgap (1.4 eV) than that of the materials above, partially block the light transmitted by the Al_{0.2}Ga_{0.8}As top subcell (1.7 eV) that should be absorbed by the Si bottom subcell (wavelengths from 720 to 850 nm). Thereby, the parasitic absorption in the GaAs intermediate

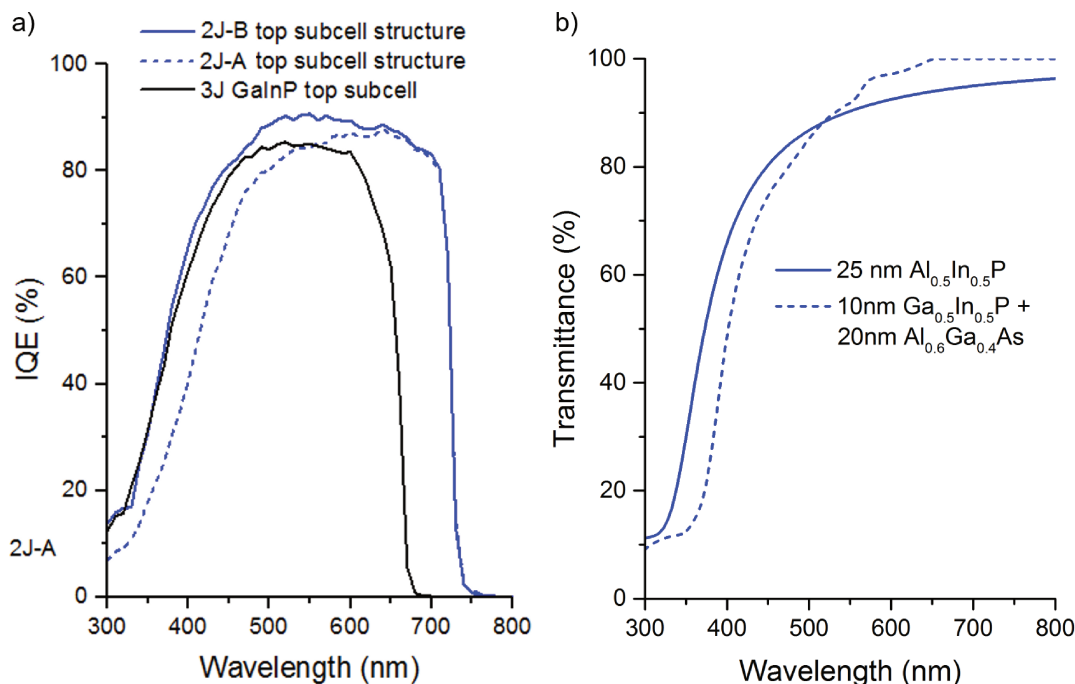


Fig. 3.2 a) *IQE* of 3J and 2J top subcells with different structures. b) Transmittance through the window layers calculated with equation 1.1. The absorption coefficients are taken from Sopra database [187].

layers reduce the photo-generated current in the bottom subcell. In figure 3.3a, the light intensity absorbed by a GaAs layer is calculated using equation 1.1. As can be seen, the severity of this loss greatly depends on the layer thickness, making a thin GaAs bonding layer more advantageous.

The CMP treatment used to obtain smooth surfaces, required for wafer bonding, is also beneficial in order to reduce the GaAs bonding layer thickness. The GaAs thickness after CMP is measured by ellipsometry, a characterization technique based on the measurement of polarization change upon light beam reflection and interaction with the material structure. Figure 3.3b shows the bottom subcell *IQE* of different 2J tandem cell realizations with different GaAs intermediate layer thicknesses. The total thickness of the GaAs intermediate layers for the 2J-A structure is 550 nm, including the GaAs bonding layer of 500 nm and the two 25 nm GaAs layers of the tunnel junction. For Sample 2J-A (with 2J-A structure), CMP was used before bonding to reduce the total GaAs thickness to 225 nm. Structure 2J-B, has an initial GaAs bonding layer thickness of 100 nm and the tunnel junction only contains one GaAs layer of 25 nm. For Sample 2J-B (with 2J-B structure), this initial GaAs thickness of 125 nm was reduced by CMP to 85 nm. Taking only into account the 720 to

850 nm wavelength range, Sample 2J-B presents an improvement of 3.6% in bottom subcell I_L with respect to Sample 2J-A.

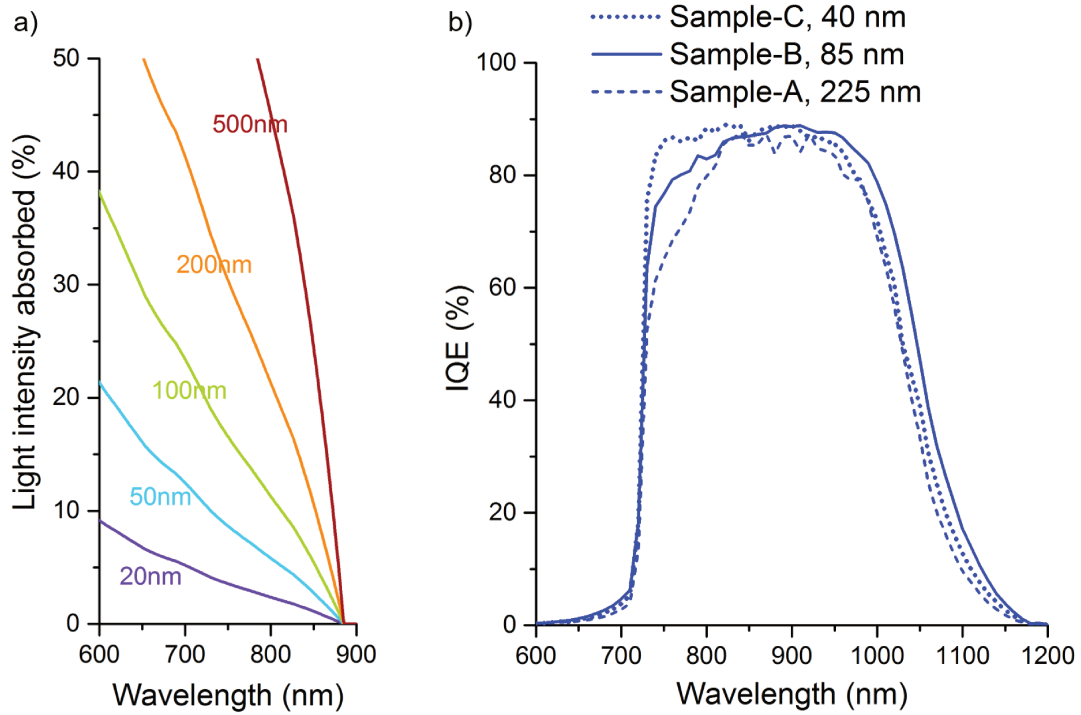


Fig. 3.3 a) Light intensity absorbed by a GaAs layer of different thicknesses as a function of wavelength, calculated with equation 1.1. The absorption coefficients are taken from Sopra database [187]. b) Experimental IQE of 2J bottom subcells. The GaAs interfacial layer thickness (including the bonding layer and tunnel junction) was measured by ellipsometry after CMP.

In order to further reduce absorption losses in the GaAs intermediate layers, structure 2J-B was slightly modified by using a fully AlGaAs tunnel junction (structure 2J-C). Sample 2J-C (with 2J-C structure), had a GaAs thickness after CMP of only 40 nm, resulting in a bottom subcell I_L improvement of 6.8% with respect to Sample 2J-A. The use of a higher bandgap material for the bonding layer could completely eliminate the absorption losses in the intermediate layers, but this would require the development of a new III-V//Si wafer bonding technique adapted for this material.

3.2 Si bottom cell design and fabrication

In order to obtain current-matching in 2T series-connected MJSC, the design of the Si bottom subcell is as important as the top. The Si bottom subcell typically limits indeed the current of 3J 2T III-V on Si MJSC, as reported by other groups [81, 144, 174, 188, 189] and also shown by our 3J cells [154, 166]. The reasons are the indirect bandgap of Si with a lower absorption coefficient and the incompatibilities of conventional well-established Si single-junction fabrication processes with III-V on Si integration. For wafer-bonded tandem cells, this includes not being able to use Si front surface texturing and a limited thermal budget to prevent degradation of III-V upper layers.

Some of the requirements on the Si bottom subcell for wafer-bonded highly efficient III-V on Si MJSC are: a clean and smooth front Si surface to enable wafer bonding; good front surface passivation to prevent recombinations at the often damaged III-V//Si interface; and enhanced infrared response, since only long wavelengths transmitted by the upper layers can be absorbed.

3.2.1 Si cell technologies

The most common Si cell technologies reported in the literature are reviewed in this section, including front and rear surface passivation and the substrate choice. Its compatibility with the III-V on Si integration processes and its feasibility using CEA equipment are also discussed.

3.2.1.1 Substrate

As shown in figure 1.10, Si solar cells made of single crystalline substrates are the most efficient. Single crystalline wafers are manufactured by two main processes: Czochralski (CZ) [190] and Float Zone (FZ) [191]. CZ wafers are the most used for both commercial PV and integrated circuit industry. However, this kind of wafers are not well adapted for high efficiency solar cells because they contain a large amount of oxygen (10^{18} cm^{-3}). Oxygen in boron-doped p-type CZ wafers can create B-O recombination centers under illumination that degrade minority carrier lifetime [192, 193]. In addition, annealing may produce thermal donors or activate metallic lifetime-killing impurities [194], making the wafers sensitive to high temperature processing.

To overcome some of these problems, the use of FZ wafers is preferable for high efficiency solar cells [191]. FZ substrates are highly pure, with extremely low oxygen concentration and thus are typically used for laboratory cells. However, commercial use is less common

due to the difficulty of growing large diameter ingots and their higher cost [195]. High quality FZ substrates are preferred for III-V on Si applications to enhance Si bottom subcell performance and also because Si wafer cost is low, even for FZ, compared to the expensive GaAs substrate.

3.2.1.2 Front surface

Since the Si surface needs to be flat and smooth to enable wafer bonding, this restricts the possible front surface architectures and compatible processes. In addition, as explained in chapter 2, the bonding interface is damaged due to ion bombardment used in SAB, producing an amorphous interlayer. The recombination at this interface is high, which can reduce V_{OC} and thus good front surface passivation is required.

III-V//Si interface passivation using dielectric layers, as in the Passivated Emitter Rear Cell (PERC) structure [196], is difficult to implement. Since there are no metal contacts in the Si surface, the passivation layers, which are electrical insulators, should be deposited in all the surface, thereby preventing majority carrier flow.

For this reason, in this study a full area emitter design is chosen forming an n-on-p homojunction Si solar cell. The n^+ emitter is performed by thermal diffusion or implantation of phosphorous dopant atoms and activated using different annealing processes, as will be detailed in section 3.2.2. For single-junction Si cells, the ideal emitter is obtained through the trade-off existing between high doping to passivate the area below the contacts where surface recombination velocity (SRV) is high and low doping in passivated areas where SRV is low in order to minimize lifetime degradation due to doping-induced defects. In the case of wafer-bonded III-V on Si tandem cells, a high SRV is expected in the full area due to defects produced at the III-V//Si interface, specially for the SAB technique in which ion bombardment is used. In addition, as already explained in chapter 2, high surface doping is also recommended in order to favor conduction through the III-V//Si interface.

Only very recently, a full area passivation technique compatible with III-V on Si integration was reported using doped poly-Si and ultra-thin (1.2 nm) tunnel SiO_2 layers [79, 197]. This structure provides an excellent surface passivation for planar surfaces by suppressing the recombination of minority carriers and at the same time allowing majority carrier conduction. CEA is also working in this kind of passivation [198] and III-V on Si solar cells using this technique are currently being manufactured.

3.2.1.3 Rear surface

Rear surface passivation is specially important for Si bottom subcells used in tandem devices in order to enhance the response of infrared light (long wavelengths) that are absorbed deep inside the material and thus, close to the rear surface.

Similar to III-V cells, the most common approach for the rear-side processing in Si solar cells is the incorporation of a BSF layer. The BSF does not need to have a higher bandgap as long as it provides an adequate potential barrier for minority carriers. For n-on-p (also known as p-type) cells, this is typically done by a highly doped p^+ region that passivates the semiconductor/metal interface, keeping the electron minority carriers away and thus reducing recombinations.

Full-area Al screen printed together with alloyed rear contact is the most common approach for manufacturing p-type conventional Si solar cells, due to its simplicity and low manufacturing costs [19]. Annealing at temperatures up to 900 °C allows Al to alloy with Si, leading to the formation of a BSF. In our case, due to the high temperatures required, this process should be done before bonding in order to prevent degradation of III-V layers. However, there are incompatibilities with the wafer bonding tools and vacuum chambers, in which metal contamination is not allowed. Therefore, this conventional process is not compatible with III-V on Si integration tools used at CEA.

Since a highly doped full area BSF can degrade lifetime, the passivation with an amorphous Si (a-Si) layer was also considered, as in the Heterojunction with Intrinsic Thin layer (HIT) cells [199, 200]. This approach usually consists in depositing thin hydrogenated a-Si (a-Si:H) layers on the p-type c-Si (figure 3.4a), which reduces surface dangling bonds and forms a BSF thanks to the effective higher bandgap of a-Si. High-quality a-Si:H layers can be deposited by Plasma-Enhanced Chemical Vapor Deposition (PECVD) at temperatures below 250 °C, which is an excellent alternative to keep the thermal budget of the III-V/Si structure to a minimum. The major disadvantage is that a-Si recrystallizes at 300 °C, thus losing its passivation effect. Therefore, a-Si cannot be deposited before the front metal contacts, since they are annealed at 395 °C to form an ohmic contact with the III-V surface. However, a-Si cannot be deposited after the metal contacts neither, because samples containing III-V materials and metal are not allowed in CEA a-Si deposition chambers due to contamination issues. Thereby, this approach could neither be implemented at CEA.

Another possibility is rear passivation with locally diffused BSF, as in the Passivated Emitter with Rear Locally diffused (PERL) structures [201]. Rear-surface passivation is obtained by dielectric layers, usually SiO_2 [202] or Al_2O_3 [203] capped by Si_3N_4 , which are deposited by PECVD or Atomic Layer Deposition (ALD) at temperatures below 350 °C [204],

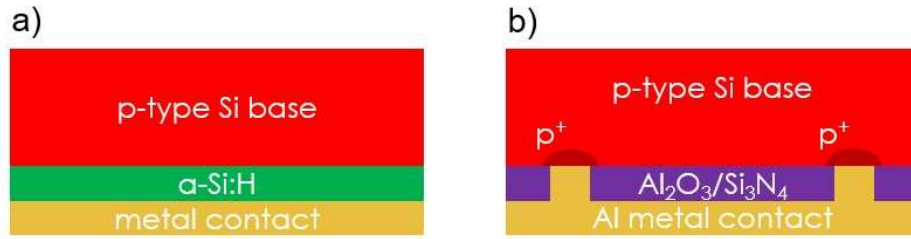


Fig. 3.4 Schemes of rear side passivation strategies reported in the literature (front surfaces are omitted), using a) a-Si:H as in HIT cells and b) $\text{Al}_2\text{O}_3/\text{Si}_3\text{N}_4$ with local p^+ BSF as in PERL structure. These approaches could not be implemented in this study.

thus allowing to perform this process after wafer bonding. Metalization by Al evaporation is then performed and point metal contacts are created by laser firing [205], which are at the same time passivated by the formation of a local Al-BSF, as shown schematically in figure 3.4b.

However, at CEA, the laser-firing process was not available and therefore, for the first realizations, a full area p^+ BSF, figure 3.5a, was performed by boron thermal diffusion or implantation processes in a similar way as the phosphorous-doped n^+ emitter. An alternative for laser-fired point metal contacts was developed using instead photolithography to locally etch the $\text{SiO}_2/\text{Si}_3\text{N}_4$ passivation layers, followed by metal pulverization, figure 3.5b. However, this process does not create a local BSF and therefore a full area BSF is still needed.

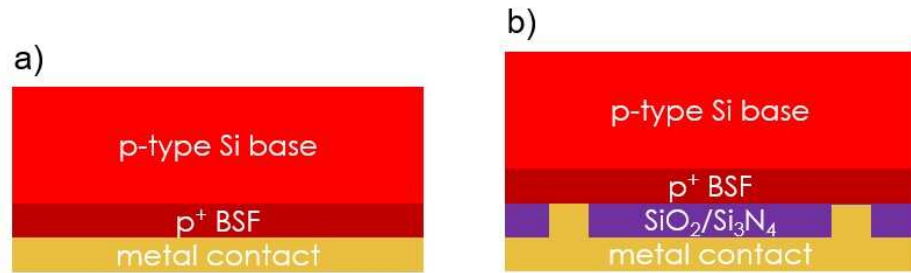


Fig. 3.5 Schemes of rear side passivation approaches performed in this study (front surfaces are omitted), using a) full area BSF, performed by thermal diffusion or implantation, and b) $\text{SiO}_2/\text{Si}_3\text{N}_4$ passivation layers in addition to the full area BSF.

Another strategy to enhance Si weak near-bandgap absorption, due to its indirect bandgap, is the use of photon recycling or light trapping techniques that increase the optical path and thus the absorption probability of long wavelength photons. High-efficiency Si solar cells commonly use random pyramids in the front surface. However, structuring the front side is not compatible with the bonding process and, even though rear side texturing could be possible

[206], it increases the complexity of the overall process flow and some incompatibilities could arise due to the non planar surface. The full sheet metal layer typically used as the back contact can act as an effective reflector, but it does not produce oblique light and thus the optical path is lower than with surface texturing. More sophisticated techniques have recently been implemented using rear-side diffraction gratings [79, 207–209].

3.2.2 Emitter and BSF formation in the Si cell

Different Si bottom subcell technologies have been discussed in the previous section. In this work, Si n-on-p homojunction subcells with a full area n^+ emitter and a p^+ BSF are fabricated due to its compatibility with III-V on Si integration and its availability at CEA. In this section, the different emitter and BSF fabrication processes performed to optimize the Si subcell are detailed.

CZ and FZ boron-doped p-type substrates of 100 mm were used. The first cells were fabricated with CZ substrates, but then they were substituted by FZ wafers due to its better quality. CZ substrate resistivity is between 14 to 22 Ωcm , while for FZ, it is between 1 to 5 Ωcm , as reported by the supplier. The substrate thickness is 525 μm , the standard in the integrated circuit industry, which is required in order to avoid breaking during wafer bonding processing. However, this substrate thickness is higher than the standard 180 μm used in PV. The difference is even higher if we take as an example recent record breaking Si solar cells with thickness below 100 μm [131].

Different techniques were studied for the emitter and BSF formation in order to optimize the homojunction subcell performance, including thermal diffusion or implantation doping processes, which may be followed by thermal treatments for dopant activation. The front surface n^+ -emitter is doped with phosphorus and the rear side p^+ -BSF is doped with boron. The different doping processes used are:

- a) Thermal diffusion of POCl_3 for the phosphorous emitter formation or BBr_3 for the boron BSF at 850 °C or 950 °C respectively.
- b) Beam Line Ion Implantation (BLII) using a VIISTA[®] Applied Materials tool, followed by two separated anneals for boron and phosphorus thermal activation at 1000 °C and 850 °C respectively.
- c) Plasma Immersion Ion Implantation (PIII) using a PULSION[®] Nano IBS equipment [210] followed by a single high temperature anneal (co-anneal) at 1000 °C.

The phosphorus and boron implantation doses were between 10^{15} and $3.5 \times 10^{15} \text{ cm}^{-2}$. The thermal activation is either a single high temperature anneal (co-anneal) to activate at the same time the implanted phosphorus emitter and boron BSF, or separated anneals for boron and phosphorus activation respectively [211].

The emitter and BSF doping profiles are measured by Secondary-Ion Mass Spectrometry (SIMS), which consists in bombarding the sample surface using a focused primary ion beam, causing ejection of secondary ions by sputtering. These secondary ions are then collected and the mass/charge ratios are analyzed with a mass spectrometer to determine the surface composition. With this technique all dopants are measured, even if they are not active. The measured doping profiles are presented in figure 3.6.

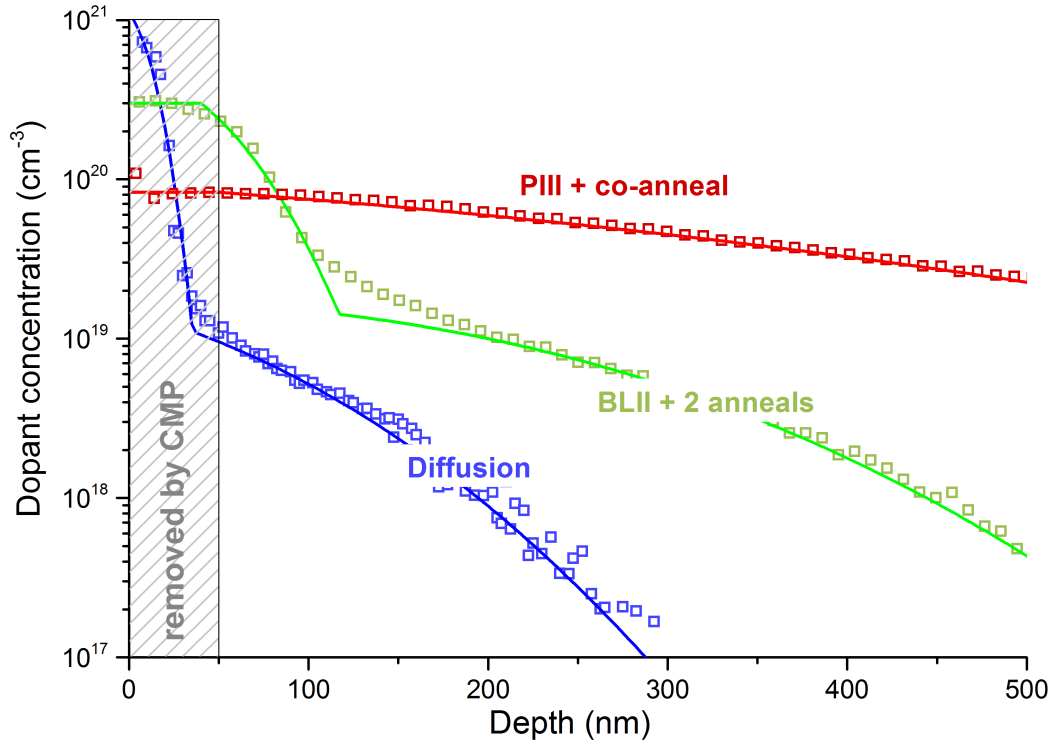


Fig. 3.6 Phosphorus dopant profiles at the Si front surface of different n^+ emitters measured by SIMS. Fit functions used for PC1D simulations are included. The first 50 nm are removed by CMP in the case of diffusion, as shown by the gray patterned zone.

Phosphorus implanted dopant profiles depend mainly on the thermal load during processing. Deeper profiles are obtained by implantation with co-anneal (red curve), but the doping level at the surface is lower compared to the cells processed with two anneals (in green) or by diffusion (in blue). Therefore, thermal diffusion or implantation followed by two anneals appear more favorable for a better surface passivation, thus reducing recombinations at the III-V/Si interface.

However, the doping profiles shown in figure 3.6 are measured before the bonding process. The CMP step, often required in order to reduce surface roughness, removes approximately 50 nm of material, which can have a great impact on the surface doping level for steep doping profiles obtained by diffusion. In addition, ion bombardment can decrease the active doping concentration [141]. Therefore, if CMP is applied, a deeper doping profile, such as the one obtained by implantation with two anneals (green curve), appear more attractive than the one obtained by diffusion because a higher surface doping level is achieved.

The decision to apply the CMP treatment before the bonding depends on the surface properties. RMS roughness produced by thermal diffusion vary from 0.3 to 1.1 nm. Therefore, CMP is often applied to assure a successful bonding. In contrast, implantation processes lead to a smoother surface with RMS roughness of 0.3 nm, thus enabling bonding without CMP.

In the next section, the substrate and fabrication process impact on the subcell performance is studied by simulations in order to understand the electrical behavior and to propose optimization strategies.

3.2.3 Design and optimization of Si bottom subcell

In this section, the Si bottom cell structure is simulated using the program PC1Dmod 6.2 [212–214] in order to optimize the design and increase its performance. PC1Dmod 6.2 is an updated version of the well known PC1D one-dimensional semiconductor device simulator [215], which latest official release was in 1997. The program uses a finite-element numerical method for solving the coupled nonlinear equations for carrier generation, recombination and transport in the device. PC1Dmod 6.2 updates include state-of-the-art models for c-Si and extended device physics by implementing Fermi–Dirac statistics. Since electrons are fermions, the Pauli exclusion principle has to be considered for carrier concentrations larger than 10^{18} cm^{-3} in order to obtain accurate simulation results [216]. This is specially relevant for the highly doped emitter region.

PC1Dmod 6.2 uses the new widely accepted parameterization for intrinsic recombination in c-Si [217], consistent with the theory of Coulomb-enhanced Auger and radiative recombination. Auger and radiative recombination are influenced by temperature, doping, and electric field, which are often fairly consistent for a given material. However, SRH lifetime depends on the level of defects in the crystal lattice and therefore it is determined using semi-empirical models that take into account doping induced defects. As shown in the following equation, SRH bulk recombination model in PC1Dmod 6.2 (and PC1D 5.9) uses a single trap energy level within the bandgap, E_T , with separate electron and hole lifetimes, τ_n

and τ_p :

$$R_{SRH} = \frac{pn - n_{ie}^2}{\tau_n(p + n_{ie}e^{-E_T/kT}) + \tau_p(n + n_{ie}e^{E_T/kT})} \quad (3.1)$$

where R_{SRH} is the RSH recombination rate, n_{ie} the effective intrinsic carrier density and p and n the hole and electron densities, which are changed through doping. τ_n and τ_p correspond to intrinsic material at a temperature of 300 K. The trap energy level is set at the middle of the bandgap and thus $E_T = 0$.

The main simulation parameters are extracted from experimental measurements of Si single-junction cells fabricated by thermal diffusion processes, detailed in section 3.2.2, using CZ or FZ substrates. This includes I - V , EQE and front surface reflectance, R . Bulk doping is taken from the substrate supplier and the doping profiles measured by SIMS, shown in figure 3.6, are fitted with complementary error functions (erfc):

$$N(x) = N_0 \operatorname{erfc}\left(\frac{x - x_p}{x_d}\right), \text{ with } N(x) = N_0 \text{ for } x < x_p \quad (3.2)$$

$$\operatorname{erfc}(y) = 1 - \operatorname{erf}(y) = 1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-t^2} dt$$

where N_0 is the peak doping, x is the depth from the surface, x_d is the depth factor and x_p is the peak position.

Reference values for bulk minority carrier lifetime, SRV and internal reflectance can be estimated by fitting the experimentally measured I - V and EQE curves, as shown in figure 3.7. The main PC1D parameters used are listed in table 3.4.

For the tandem configuration, the incident spectrum has to be filtered in order to simulate the absorption of shorter wavelengths by the III-V upper layers. Truncating the spectrum is the most direct approach, which can be easily implemented with PC1D by setting the external reflectance to 100% at the corresponding wavelengths, i.e. from 300 to 850 nm in the case of the 3J. Although this does not perfectly reproduce the slight semi-transparency of III-V layers for near-bandgap photons, as shown by the small EQE difference from 700 to 850 nm in figure 3.7a, it is a good approximation. Some of the results presented in this section are then specifically calculated for the 3J. However, the resulting optimization strategies can also be applied for the 2J bottom subcell.

In order to optimize the 3J bottom subcell design, some key parameters like bulk lifetime, cell thickness, bulk p-type doping concentration (P), Back SRV (BSRV), Front SRV (FSRV) and the emitter doping profile are modified in order to study its impact on the subcell performance.

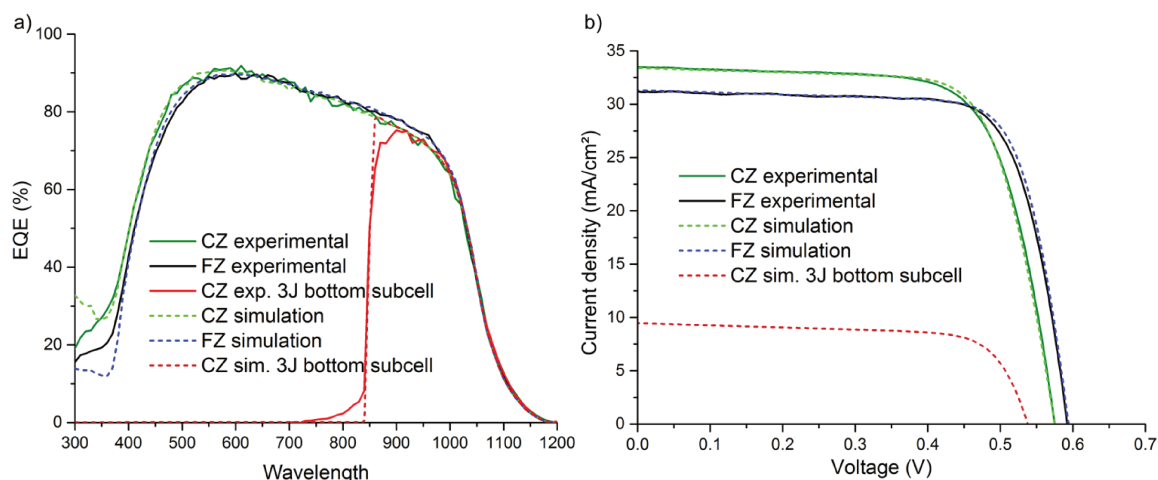


Fig. 3.7 a) *EQE* and b) *I–V* experimental curves of Si single-junction cells fabricated by thermal diffusion processes using CZ (in light green) and FZ (in black) substrates. PC1D simulated curves are also included showing good agreement, which allows to estimate the effective bulk lifetimes and SRV. The Si subcell in a 3J cell is also simulated by truncating the short wavelengths (from 300 to 850 nm) of the incident spectrum. The lower total incident light reaching the bottom subcell reduces I_{SC} and also V_{OC} .

PC1D parameter	CZ substrate	FZ substrate
Cell thickness	525 μm	525 μm
Bulk (p-type) doping (P)	10^{15} cm^{-3}	10^{16} cm^{-3}
Emitter profile (erfc)	$N_0 = 1 \times 10^{19} \text{ cm}^{-3}$, $x_d = 0.135 \mu\text{m}$, $x_p = 0 \mu\text{m}$	
BSF profile (erfc)	$P_0 = 8 \times 10^{19} \text{ cm}^{-3}$, $x_d = 0.23 \mu\text{m}$, $x_p = 0.08 \mu\text{m}$	
Bulk lifetime	80 μs	250 μs
Front SRV	$3 \times 10^5 \text{ cm/s}$	$2 \times 10^6 \text{ cm/s}$
Back SRV	0 cm/s	$1 \times 10^5 \text{ cm/s}$
External front Reflectance	experimental data: $\sim 5\%$	
Internal rear Reflectance	20%	
Spectrum	1-sun AM1.5G and truncated at 850 nm	

Table 3.4 Main PC1D simulation parameters used to fit the experimental curves of figure 3.7.

3.2.3.1 Impact of bulk lifetime and back surface recombination

First, lifetime and BSRV are studied: lifetime is varied from 80 μs , corresponding to the CZ substrates, to 1000 μs , which is the expected lifetime for FZ substrates reported by the supplier. The estimated low effective lifetime of 250 μs found in our cells can be explained

due to degradation during cell fabrication processes, as will be discussed in section 3.2.4.2. BSRV is varied from 0 to 10^7 cm/s. The other parameters are the same as for the FZ single-junction fit and are kept constant.

The resulting I - V and IQE simulated curves are presented in figure 3.8. For $\tau = 80\mu\text{s}$, V_{OC} is limited by bulk recombination and hence BSRV has not a big impact on IQE . This explains the effective BSRV value of 0 cm/s set for the CZ fit, already presented in table 3.4. With $\tau = 1000\mu\text{s}$, I_{SC} increases due to much better IQE performance at long wavelengths. Low energy photons absorbed deeper in the base can now be collected before recombining. The cell is then limited by surface recombination, as can be seen by the impact of BSRV in both I_{SC} and V_{OC} .

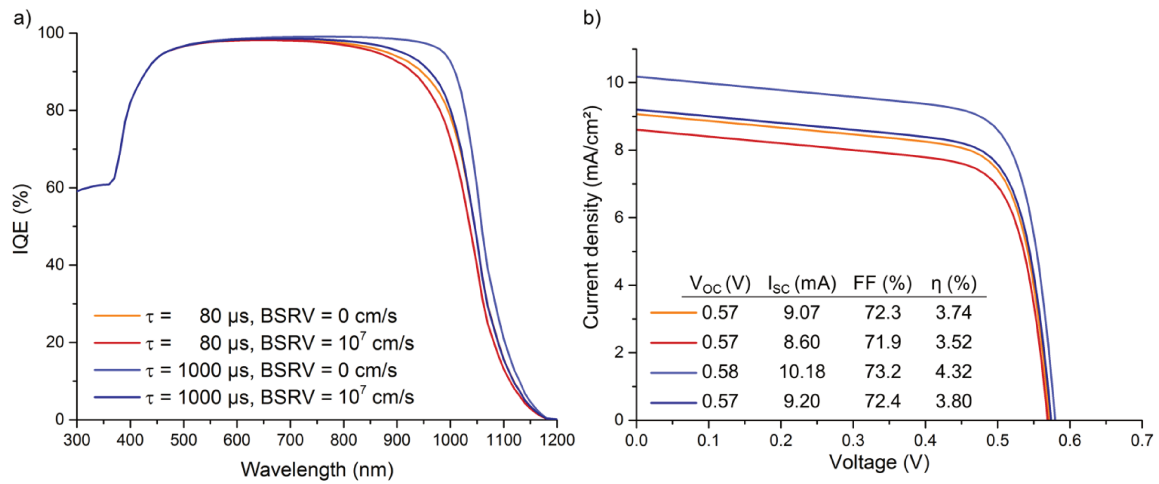


Fig. 3.8 a) IQE and b) I - V simulated curves for different lifetimes (τ) and BSRV. For the I - V curves, short wavelengths from 300 to 850 nm are truncated from the AM1.5G incident spectrum, as in the 3J Si bottom subcell.

3.2.3.2 Impact of Si cell thickness

The effect of cell thickness on cell performance is also studied. As already explained, the 525 μm thickness is required to avoid breaking during wafer bonding processing. However, wafer bonded III-V on Si tandem cells were reported using a Si bottom substrate of only 300 μm [144]. Cell thickness is then varied from 300 to 525 μm for low and high lifetimes (80 – 1000 μs as before). BSRV is set to 0 and the other parameters are not changed.

The resulting I - V and IQE simulated curves are presented in figure 3.9. Reduction of cell thickness could be beneficial in the case of low lifetime in order to enhance collection, as can be seen by the 850–1000 nm IQE improvement. However, losses due to poor absorption

for wavelengths above 1000 nm counter this effect and the resulting I_{SC} is reduced. Since for a high lifetime of 1000 μ s photo-generated carriers can be collected no matter how deep they are produced, a thinner cell is not beneficial in this case and only reduces absorption for wavelengths above 950 nm. Therefore, a thick solar cell combined with high lifetime enhances infrared response. However, a better strategy for a moderate lifetime would be to use a thin cell combined with reduced BSRV and light trapping techniques that increase the optical path of photons and thus collection efficiency [79]. This is illustrated by increasing the rear internal reflectance (int. R) to 90% for the red dashed curve. As can be seen in the simulation, this has a big impact on IQE values for long wavelengths and thus on I_{SC} .

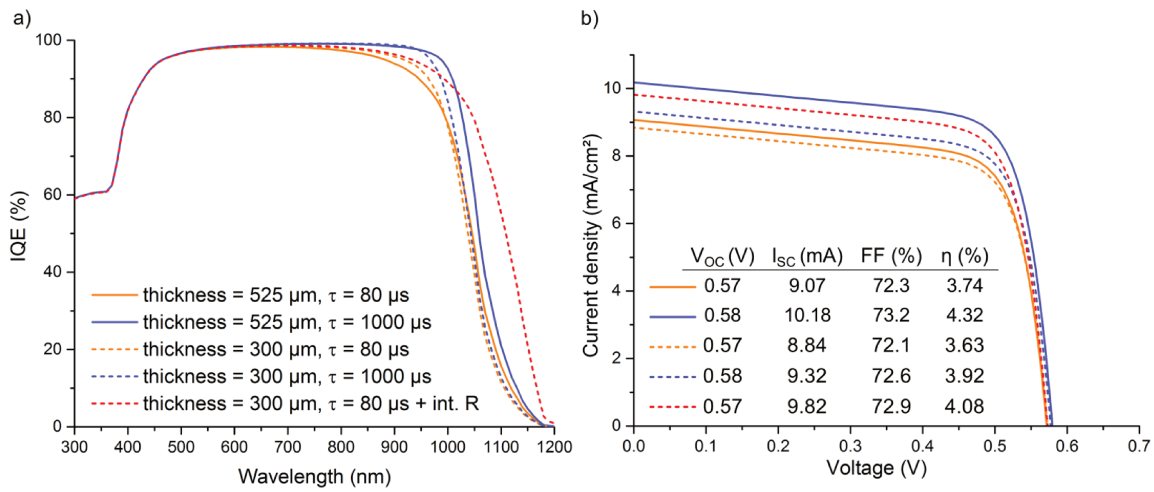


Fig. 3.9 a) IQE and b) $I-V$ simulated curves for different cell thickness and lifetimes (τ). Rear internal reflectance (int. R) is increased to 90% for red dashed curve. For the $I-V$ curves, short wavelengths from 300 to 850 nm are truncated from the AM1.5G incident spectrum, as in the 3J Si bottom subcell.

3.2.3.3 Impact of emitter and front surface recombination

The impact of FSRV is analyzed together with the different emitter doping profiles obtained by diffusion, PIII and BLII, removing or not the top 50 nm corresponding to CMP treatment. FSRV is varied from 0 to 10^7 cm/s, τ is set to 1000 μ s and the other parameters are kept constant as before.

The resulting $I-V$ and IQE simulated curves are presented in figure 3.10. Comparing the solid and dotted blue curves (0 versus 10^7 cm/s FSRV) it can be seen that FSRV does not affect significantly the I_{SC} because the light incident on the 3J and 2J bottom subcells, transmitted by the III-V upper layers (wavelengths above 850 nm for the 3J and above 720 nm

for the 2J), is absorbed deeper in the material and thus closer to the p-n junction than to the front surface, allowing collection of photo-generated carriers. FSRV only degrades significantly IQE for wavelengths below 700 nm. However, high FSRV seriously degrades V_{OC} , showing the importance of passivating the front surface.

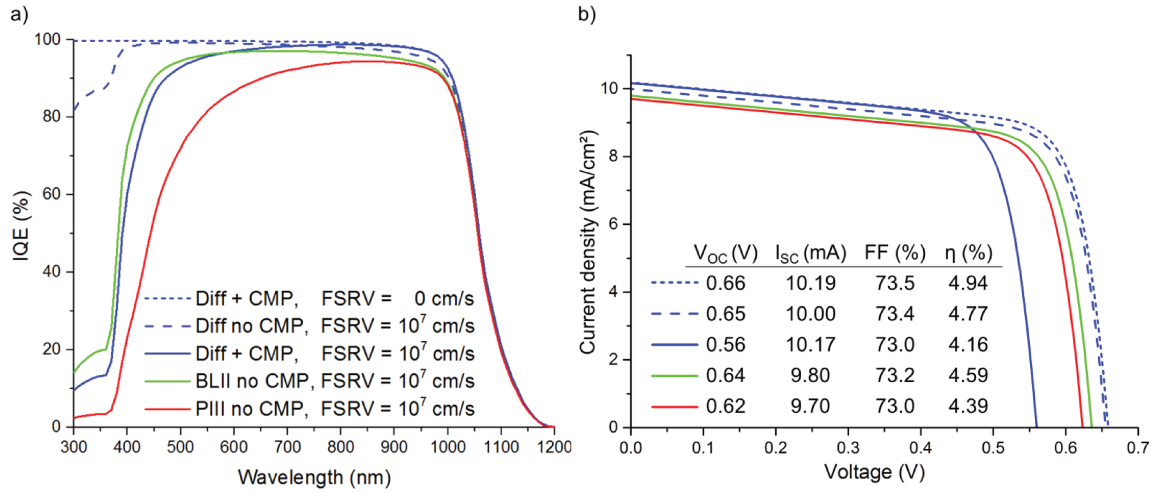


Fig. 3.10 a) IQE and b) I - V simulated curves for different emitter doping profiles and FSRV. For the I - V curves, short wavelengths from 300 to 850 nm are truncated from the AM1.5G incident spectrum, as in the 3J Si bottom subcell.

The diffusion profile when CMP is applied produces the lowest V_{OC} , indicating a poor front surface passivation that can be explained by its low surface doping level, as can be seen in figure 3.6. The CMP produces nonetheless a slight IQE improvement because it makes the doping profile more shallow. PIII profile produces the worst IQE performance, specially for short wavelengths, but some degradation is also produced in the 3J and 2J bottom subcell absorption range, obtaining hence the lower I_{SC} . This might be because of the higher depth of the PIII emitter profile, which produces lifetime degradation due to doping induced defects. In contrast, the diffusion profile without CMP is ideal because it has a high surface doping level and is shallow, passivating the surface and limiting at the same time lifetime degradation due to high doping. The V_{OC} obtained is almost as high as in the case without FSRV, which shows its good surface passivation. BLII emitter produces a lower V_{OC} compared to the diffusion profile without CMP, corresponding to its lower surface doping level. A slightly IQE degradation can also be seen for wavelengths above 700 nm due to its higher depth.

In conclusion, bulk lifetime is the first limiting factor of the Si subcell when using 525 μm thick wafers and therefore high quality FZ substrates are needed. Bulk lifetime affects both

the V_{OC} and I_{SC} . A thick solar cell combined with high lifetime enhances infrared response, but for moderate lifetimes a thinner cell combined with reduced BSRV and light trapping techniques is a better option. For high bulk lifetime or thin cells, the performance is limited by the back and front SRV. BSRV affects both V_{OC} and I_{SC} , while FSRV only degrades the V_{OC} . Similar to the FSRV, the emitter impact on V_{OC} is greater than on I_{SC} , thanks to the absorption of shorter wavelength photons on the III-V upper layers, as was already reported [188, 218]. In the case of III-V//Si interfaces with high FSRV, an emitter with a highly doped surface is critical to achieve good surface passivation and to maximize V_{OC} , outweighing the drop in I_{SC} due to lifetime degradation. Therefore, CMP treatment should be avoided when possible because it removes the highly doped superficial material, highlighting the advantage of implantation processes that allow bonding without CMP.

3.2.4 Experimental analysis of substrate and subcell performance

PC1D simulations have allowed to identify the key factors that limit Si subcell performance, being the bulk lifetime the most critical characteristic that needs to be improved. In this section, substrate lifetime through the different Si cell fabrication steps is analyzed experimentally. First, the initial bulk lifetime of CZ and FZ substrates is measured. Then, the impact of thermal diffusion and implantation processes is studied and finally, the Si subcell IQE of fabricated tandem cells is analyzed.

3.2.4.1 Initial substrate minority carrier lifetime

Minority carrier lifetime is experimentally measured at 300 K by Quasi-Steady-State Photo-Conductance (QSSPC) [219] with a Sinton WCT-120 equipment. In this technique, carriers are generated by illuminating the semiconductor material with a short light pulse. This increases the conductivity and thus Δn decay with time can be determined. The longer the minority carrier lifetime, the more slowly the carriers decay. Lifetime was also determined locally using Microwave detected Photo-Conductance Decay (μ -PCD) with a SEMILAB WT1000 equipment. This technique is similar to QSSPC but in this case Δn decay with time is determined by measuring the microwave reflectance, which is a function of conductivity. The measured values correspond to the effective carrier lifetime, τ_{eff} , which as described by equation 3.3, is the combination of surface and bulk recombination.

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{1}{\tau_{surface}} \quad (3.3)$$

A simple way to approximately measure τ_{bulk} , is by correctly passivating the surfaces, so that $1/\tau_{\text{surface}}$ is negligible and hence the measured τ_{eff} is approximately equal to τ_{bulk} [220]. Passivation in this study is performed by Si_3N_4 , $\text{SiO}_2/\text{Si}_3\text{N}_4$ or $\text{Al}_2\text{O}_3/\text{Si}_3\text{N}_4$.

Thanks to μ -PCD measurements, local iron concentration, $[\text{Fe}]$, was also determined by measuring the lifetime variation under illumination as a function of time, as described in reference [221]. Light transforms the chemical state of non-precipitated iron from FeB pairs to interstitial Fe. This way, $[\text{Fe}]$ can be determined from the final stabilized lifetime and the initial value, which is measured after storing the samples in the dark.

Experimentally measured effective minority carrier lifetimes and iron concentrations for CZ and FZ substrates are presented in table 3.5. Double side Si_3N_4 passivation was performed in order to reduce surface recombination.

Substrate	$[\text{Fe}]$ (cm^{-3})	τ (μs)
CZ	4.1×10^{11}	110
FZ	1.5×10^{10}	780

Table 3.5 Minority carrier lifetime, τ , and iron concentration, $[\text{Fe}]$, for CZ and FZ Si substrates whose surface is passivated with thin layers of Si_3N_4 . Values of τ correspond to a carrier injection level of $\Delta n = 10^{15} \text{ cm}^{-3}$.

As expected, FZ substrates have better initial lifetime than CZ. A possible reason is the large amount of oxygen often present in CZ substrates that, as already introduced in section 3.2.1, create B-O recombination centers in boron-doped p-type CZ wafers [192, 193]. In addition, the high iron concentration found could also degrade lifetime [194]. FZ wafers are then used for the rest of this study due to its better quality.

Both lifetime measurement results are higher than the values extracted from the I - V and EQE curve fit of 1J Si cells presented in figure 3.7 (80 and 250 μs for cells made of CZ and FZ respectively). This already suggests a possible bulk lifetime degradation during the cell fabrication, as will be confirmed in the next section. Consequently, it is very important to fully characterize Si minority carrier lifetime during the fabrication process and the possible activation of iron impurities.

3.2.4.2 Impact of diffusion and implantation processes

Lifetime and iron concentration measurements of FZ substrates, after being doped by thermal diffusion or implantation processes, are presented in table 3.6. First, thermal diffusion is studied by doping with the same element, boron or phosphorous, on both sides of the wafer

and is compared with the actual n-p cell structure using phosphorous for the front surface, to create the n^+ -emitter, and boron on the rear side to form the p^+ -BSF.

Dopant	Doping technique	[Fe] (cm^{-3})	τ (μs)
double-side boron	diffusion 950 °C	5.3×10^{12}	30
double-side phosphorous	diffusion 850 °C	9.1×10^9	860
boron + phosphorous	diffusion 950/850 °C	-	85
boron + phosphorous	Beam Line Ion Implantation (BLII)	1.1×10^{12}	205

Table 3.6 Minority carrier lifetime, τ , and iron concentration, [Fe], for FZ substrates doped by thermal diffusion or implantation processes. Wafers prepared by diffusion are passivated by $\text{SiO}_2/\text{Si}_3\text{N}_4$, while the implanted sample is passivated by $\text{Al}_2\text{O}_3/\text{Si}_3\text{N}_4$. Values of τ correspond to a carrier injection level of $\Delta n = 10^{15} \text{ cm}^{-3}$. This data was already published in [222].

Double-side boron diffusion severely degrades the lifetime of FZ substrates, presenting a value of only 30 μs . The iron concentration is correspondingly very high, 5.3×10^{12} , suggesting a possible activation of metallic impurities as the cause for the low lifetime [194]. In contrast, double-side phosphorus diffusion did not degrade the minority carrier lifetime, having even a slightly higher value than FZ substrates without processing (860 vs 780 μs) and lower iron concentration. The different surface passivation (Si_3N_4 vs $\text{Al}_2\text{O}_3/\text{Si}_3\text{N}_4$) could be the reason of the higher performance. Combination of boron and phosphorus diffusion is less detrimental than boron diffusion only. This can be explained by the gettering effect of phosphorus diffusion, in which some specific annealing conditions can give rise to the formation of oxygen precipitates that trap unwanted metal impurities, improving the purity of surrounding silicon [223].

Beam line implantation of boron on the rear-side together with phosphorus on the front-side presents a higher lifetime than their diffused counterparts (205 vs 85 μs). However, it is far from the original substrate lifetime, thus the full Si cell performance potential cannot be achieved.

Further lifetime improvement is expected by limiting the amount of iron metallic impurities, that can become active during high temperature steps. One direct approach towards reduction of activated iron impurities is the decrease of thermal load applied during the processing. However, high temperatures are needed in both thermal diffusion and implantation processes for doping activation. A second approach would be the use of n-type Si substrates instead of p-type because they are less sensitive to FeB pairs and interstitial Fe [221]. Nevertheless, as already exposed in section 3.1.2, an n-type substrate for a p-on-n

configuration would imply the use of a low performance window layer for the III-V top subcell due to the problems related with p-type AlInP.

In conclusion, boron diffusion is especially detrimental for substrate lifetime. Doping implantation process combining both boron and phosphorous present higher performance than its diffusion counterpart. However, the presence of iron metallic impurities, which are probably activated during high temperature steps, still limit the performance of the Si subcells.

3.2.4.3 Experimental Si subcell quantum efficiency results

IQE curves of Si bottom subcells fabricated by thermal diffusion or implantation processes, using CZ or FZ substrates, with or without CMP and SiO₂/Si₃N₄ back surface passivation are presented in figure 3.11. Only wavelengths over 900 nm are shown in order to easily compare the results from Si cells in a 3J, 2J or even 1J configuration.

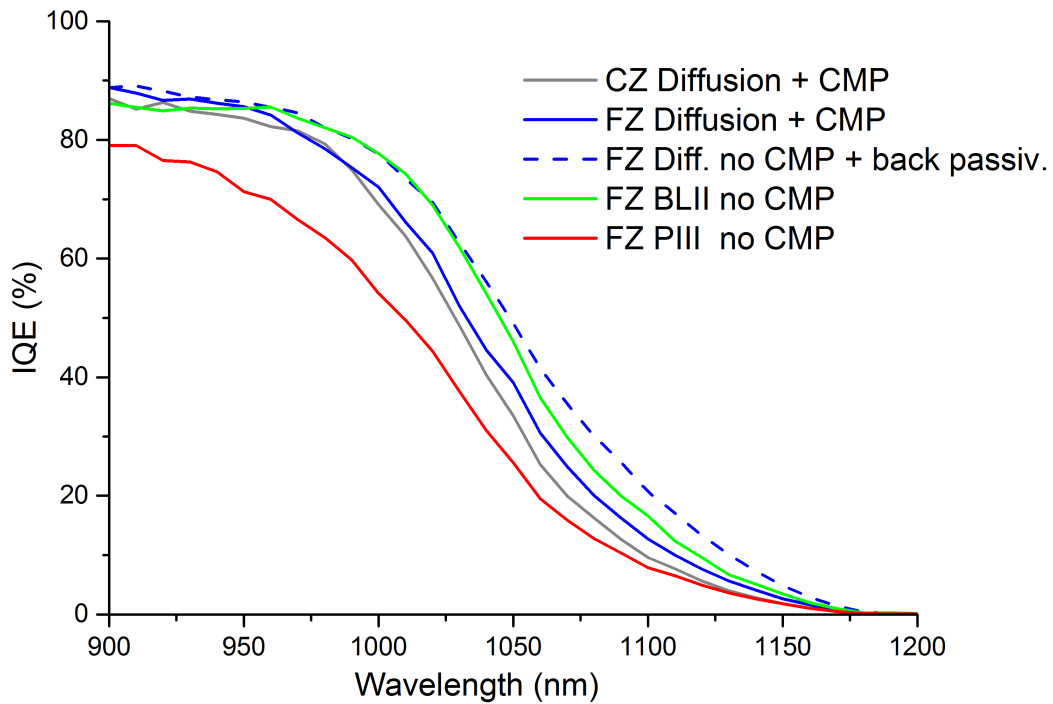


Fig. 3.11 Experimental *IQE* curves of Si bottom subcells fabricated by thermal diffusion or implantation processes, using CZ or FZ substrates, with or without CMP and SiO₂/Si₃N₄ back surface passivation. Only wavelengths above 900 nm are shown.

The subcell fabricated by PIII with co-anneal, using a FZ substrate, has the lower *IQE* signature, even worst than the cell prepared by thermal diffusion on CZ substrates. This was

predicted by the simulations presented in section 3.2.3 and can be explained by the deeper doping profile, already shown in figure 3.6, that degrades bulk lifetime due to doping induced defects.

The performance of the Si subcell fabricated by thermal diffusion, using FZ substrates, slightly improves when compared with the same diffusion process on CZ substrates, being far from the great improvement expected for a 1000 μs lifetime. These *IQE* measurements are therefore in accordance with the 85 μs effective lifetime experimentally measured after diffusion processes, already presented in table 3.6.

The subcell fabricated by BLII with 2 anneals, using also FZ substrates and without CMP, presents better performance than the diffusion process with CMP, in accordance with the measured higher lifetime of 205 μs , which counteracts the degradation produced by the deeper doping profile. This shows that implantation processes are more favorable than thermal diffusion, even if the doping profile is deeper, thanks to the lower degradation of bulk lifetime.

The cell fabricated by diffusion without CMP and using a $\text{SiO}_2/\text{Si}_3\text{N}_4$ back surface passivation improves considerably compared to its diffusion counterparts without passivating layers. In addition, the passivated cell is slightly better than the BLII subcell for wavelengths above 1050 nm, even if its bulk lifetime is probably lower. This highlights the importance of back surface passivation in order to enhance infrared performance. The combination of BLII and back surface passivation is expected to further improve the performance at long wavelengths.

IQE experimental curves confirm the Si subcell performance predicted by effective lifetime measurements and agree with the trends observed with PC1D simulations. However, to further optimize the subcells and to increase the comprehension of the fabrication process impact on performance, it would be useful to complete the *IQE* experimental analysis with spectral electroluminescence, $\text{EL}(\lambda)$, characterization. This technique would enable to measure the individual subcell V_{OC} and the derivation of the individual subcell I – V curves [224–226]. In addition, the external radiative emission efficiency (ERE) could be then calculated, which is the best figure of merit to compare the quality of solar cells of different materials [227]. However, $\text{EL}(\lambda)$ equipment was not available at CEA.

In conclusion, we have optimized the Si subcell for wafer-bonded III-V on Si tandem cells using FZ substrates and implantation processes followed by thermal activation, which enable higher minority carrier lifetimes and smoother Si surfaces in comparison with thermal diffusion processes, thereby allowing to perform the wafer bonding without the need of CMP.

3.3 Fabrication process after wafer bonding

After wafer bonding, the GaAs substrate is removed, followed by front metalization, mesa etching to partially isolate the individual cells, contact layer etching to uncover the window and finally the ARC deposition and back metalization. Figure 3.12 presents schematically all the steps, which are enumerated and detailed in the next sections.

GaAs substrate removal

1. After wafer bonding, the GaAs substrate and GaInP etch stop layer are on top of the III-V subcell. The III-V subcell upper layers are the GaAs contact layer and window: GaInP/AlGaAs for structure 2J-A or AlInP for 2J-B and 3J structures, as already described in section 3.1.2.
2. The GaAs substrate (450 μm) is removed by wet chemical etching using SC1, aqueous solution composed of NH_4OH and H_2O_2 .
3. The GaInP etch stop layer (200 nm) is removed using $\text{HCl}/\text{H}_3\text{PO}_4$.

Front metalization

4. Photolithography is performed using the metal mask. It consists of a deposition of photoresist, light exposure and developing. The metal grid is designed for a low concentration around 10 to 20 suns with a 5% shading factor, without taking into account the bus bars as it is common for concentrator solar cells. The finger pitch is 200 μm and the finger width 10 μm .
5. Surface is deoxidized using aqueous solution with 10% of HCl followed by Ni/Ge/Au/Ti/Au/Pt (10/10/20/50/500/20 nm) metal deposition by evaporation. Ohmic contact is formed during the 1 min anneal at 395 $^\circ\text{C}$, during which Ni, Ge and Au form a eutectic system. Ti layer is used to block Au diffusion into the GaAs. The final Pt layer is used to cap the Au in order to avoid Au pulverization during subsequent dry plasma etching of $\text{Si}_3\text{N}_4/\text{SiO}_2$ mesa hard mask. As shown in figure 3.13 obtained by TEM, without this Pt cap layer, gold particles are found at the ARC/window interface, which can reduce absorption and increase surface recombination.
6. Lift-off is performed to remove the remaining photoresist and at the same time the metal above it.

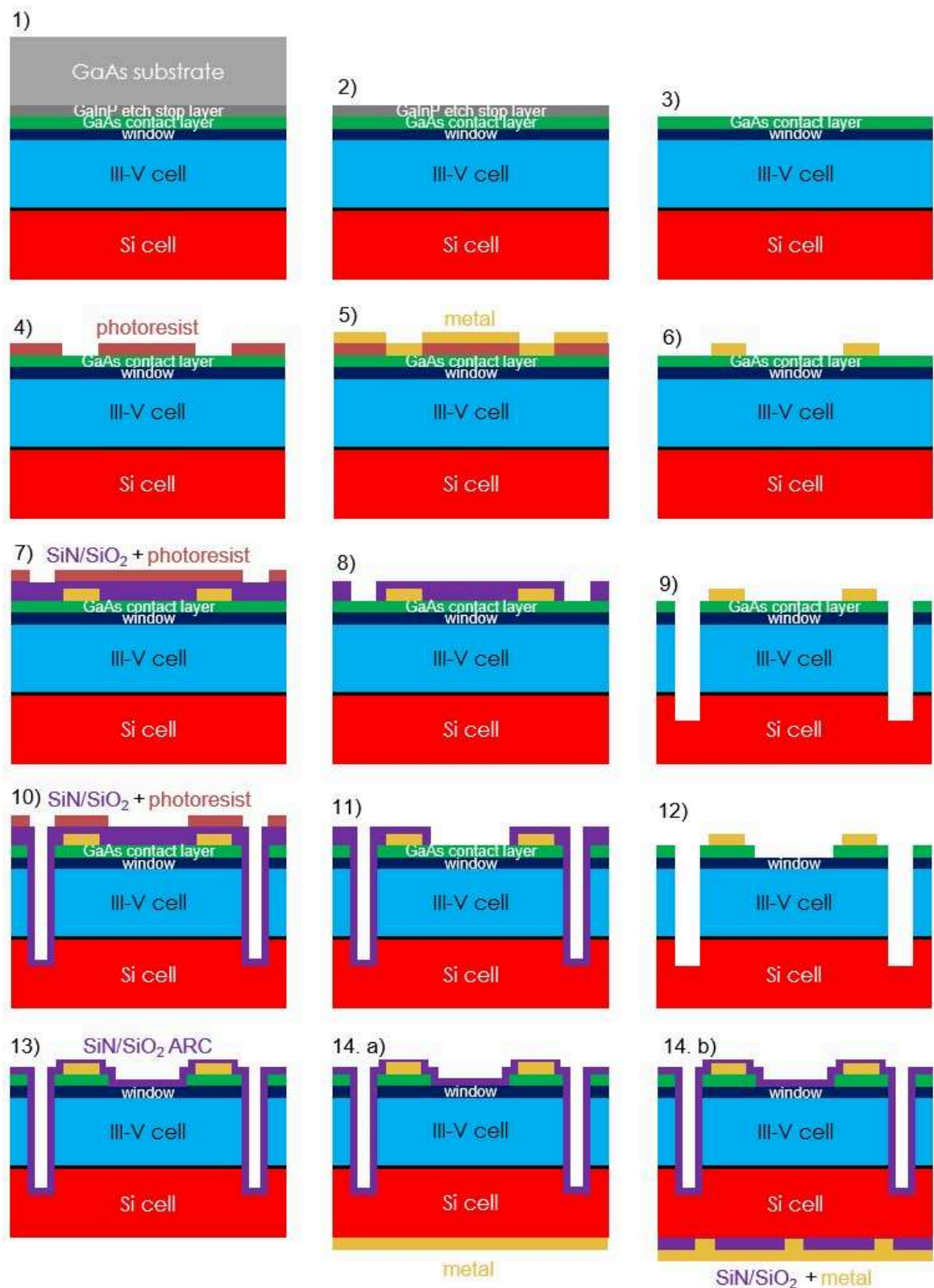


Fig. 3.12 Fabrication process flow after wafer bonding. Each step is detailed in the text.

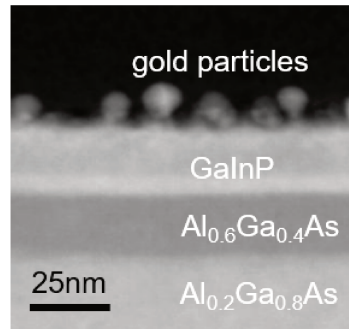


Fig. 3.13 TEM image of the front surface of a top subcell with 2J-A structure showing the presence of gold particles.

Mesa etching

7. $\text{Si}_3\text{N}_4/\text{SiO}_2$ (100/500 nm) hard mask is deposited by PECVD and photolithography is then performed using the mesa mask.
8. $\text{Si}_3\text{N}_4/\text{SiO}_2$ hard mask is etched away by Reactive-Ion Etching (RIE) followed by photoresist stripping.
9. Etching of mesa trenches by Inductively Coupled Plasma (ICP) and remaining $\text{Si}_3\text{N}_4/\text{SiO}_2$ hard mask etching by RIE. This hard mask is needed because it resists better the ICP etching than the photoresist. Mesa trenches down to 2 μm inside the Si substrate is performed to partially isolate the individual cells of 0.25, 1 and 2 cm^2 .

Mesa trenches are usually done in III-V cells in order to isolate the individual cells so that light I – V measurements on wafer can be done. However, in the case of III-V on Si tandems, mesa trenches are not effective due to the high minority carrier diffusion length in silicon, which is often above 1 mm for FZ wafers. As a consequence, photo-generated carriers produced by light impinging in the Si material outside the mesa can still diffuse to the p-n junction of the tested solar cell and increase its photocurrent [145]. Therefore, the use of a shadow mask or mechanical separation of cells by sawing is required. In this study both approaches were used.

Contact layer etching

10. $\text{Si}_3\text{N}_4/\text{SiO}_2$ (100/500 nm) hard mask is deposited by PECVD and photolithography is then performed using the window mask.
11. $\text{Si}_3\text{N}_4/\text{SiO}_2$ hard mask etching by RIE followed by photoresist stripping.

12. GaAs contact layer etching (200 nm) by SC1, followed by RIE etching of remaining $\text{Si}_3\text{N}_4/\text{SiO}_2$ hard mask. The hard mask is also more favorable in this case than the photoresist because allows a better control of wet etching.

The GaAs contact layer has to be removed in the open active areas in order to expose the window layer and prevent parasitic absorption. The GaAs contact layer is not removed under the metal contacts because it is required to form an ohmic contact, but it is not detrimental because it does not receive light. The etching process is delicate because the thin window layer could be also etched away if etching times are not carefully controlled.

In some cases, overetching of GaAs contact layer led to etching of the window. In figure 3.14 two images obtained by TEM of the front surface of III-V top subcells with Structure-B are shown. In figure 3.14a, the AlInP window is still intact, but in figure 3.14b it has been etched away and hence the Si_3N_4 ARC is directly in contact with the GaInP emitter layer. In case of degradation of window layer, front surface passivation is poor, which is demonstrated by the degradation of *IQE* at long wavelengths, shown in figure 3.14c, as already reported in literature [228]. For these reasons, a careful control of contact layer etching time is needed.

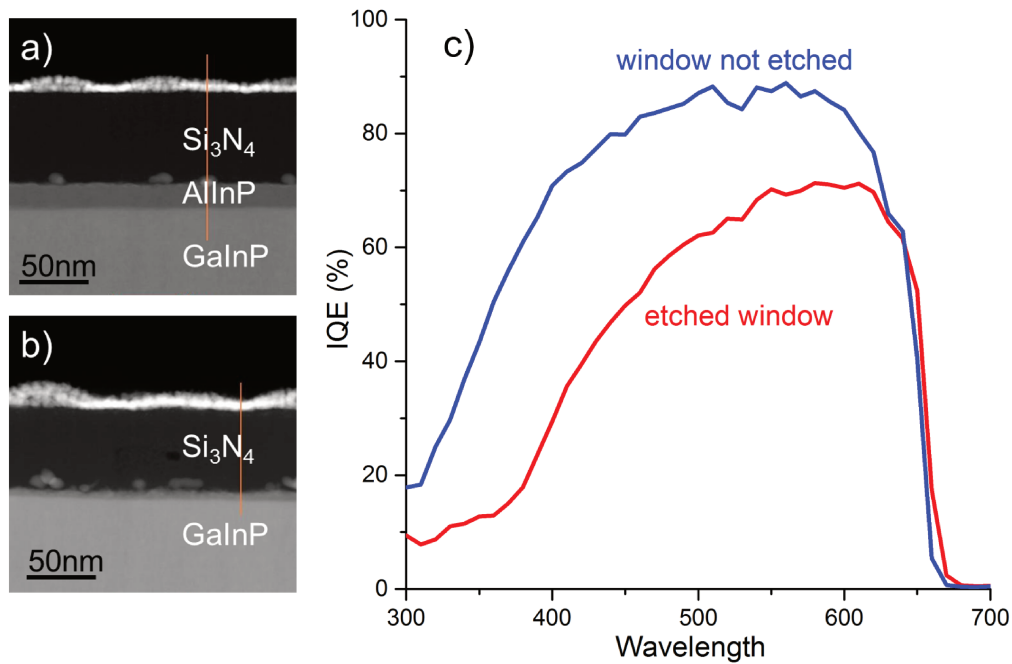


Fig. 3.14 TEM images of III-V top subcell front surface with a) the AlInP window and b) in which the AlInP window has been etched away during contact layer etching. c) *IQE* experimental curves of both cases, demonstrating the passivating role of the window.

ARC deposition

13. Si_3N_4 single-layer or $\text{Si}_3\text{N}_4/\text{SiO}_2$ dual-layer ARC deposition. Si_3N_4 is first deposited by PECVD and then SiO_2 by Ion Beam Sputtering (IBS).

If the ARC is thick, it may become difficult to have a correct contact between the front metal and the electric probes used for characterization. Therefore, ARC was etched away on top of the bus bars using the bus mask.

Back metalization and passivation

14. a) The back surface is deoxidized by dry etching and a Ti/Pt/Au (30/50/170 nm) metal layer is deposited by pulverization.
14. b) Alternatively, back surface passivation was performed as described in figure 3.5b. In this case, deposition of $\text{SiO}_2/\text{Si}_3\text{N}_4$ (5/150 nm) passivation layers by PECVD is performed followed by lithography using the back metal mask, etching of $\text{SiO}_2/\text{Si}_3\text{N}_4$ pattern by ICP, stripping and pulverization of Ti/Pt/Au metal layer. The pattern is composed of circular via separated by a distance of 500 μm , each of them with a diameter of 100 μm .

Finally, annealing during 1 min at 395 °C is performed to form ohmic metal contacts. A photo of a finished wafer is presented in figure 3.15a with individual cells comprising 0.25, 1 and 2 cm^2 . The 2 cm^2 cells are designed with a thick bus bar for an easy cell interconnection in a low concentration PV module, as the one shown in figure 3.15b [44].

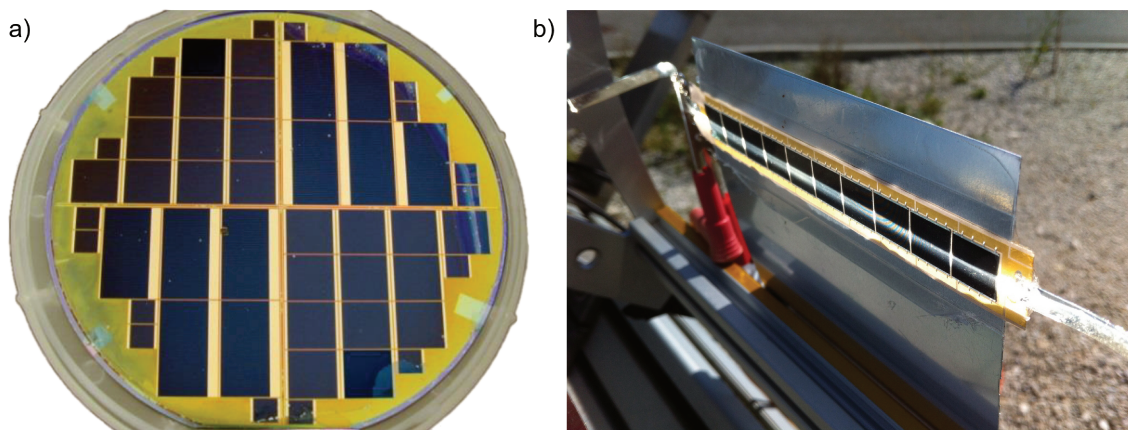


Fig. 3.15 a) Photo of a finished wafer with individual cells of 0.25, 1 and 2 cm^2 . b) cells placed in a low concentration PV module [44].

3.4 Anti-reflection coating optimization

ARC optimization is crucial in order to reduce reflection losses and hence increase EQE . All the optimizations discussed until now, focused on improving carrier collection, would be useless if most of the light does not even enter the cell due to high reflectance. In addition, ARC optimization is a simple way to minimize the current mismatching between the subcells.

Several ARC combinations have been reported in the literature for III-V MJSC and III-V//Si tandems, such as single-layers: Si_3N_4 [229, 230], SiO_2 [230]; double-layers $\text{Si}_3\text{N}_4/\text{SiO}_2$ [229–231], SiC/SiO_2 , $\text{TiO}_2/\text{SiO}_2$ [232], $\text{Ta}_2\text{O}_5/\text{MgF}_2$ [145], ZnS/MgF_2 [233–235], ZnS/SiO_2 [236] and triple-layers: $\text{SiC}/\text{HfO}_2/\text{MgF}_2$, $\text{TiO}_2/\text{HfO}_2/\text{MgF}_2$ [232]. However, at CEA, the only available materials were Si_3N_4 and SiO_2 .

CEA first cell realizations, used a single-layer Si_3N_4 ARC of 65 nm. This is optimized to reduce reflectance in the 1.7 eV AlGaAs top subcell, but is not adapted to the full 300–1200 nm absorption range of III-V on Si tandems. Therefore, in this study, the reflectance for different Si_3N_4 and SiO_2 thicknesses is simulated in order to find the most favorable double-layer ARC for the 2J and 3J tandem cell configurations.

Reflectance simulations were performed using the transfer-matrix method with an in-house program. Reflectance is affected by the cell upper layer properties, like their thicknesses and refractive index [237, 231]. Therefore, the top layers of the 3J and 2J devices are simulated, approximating their properties with available optical constants. The refractive index are extracted from Sopra database [187]. The inputs for the program are then the upper layer material properties and also an initial EQE experimental measurement of the cell, which is used to calculate the resulting EQE after addition of the ARC layers. As a result, the reflectance and EQE with the additional ARC layers are simulated, which can be used to calculate the J_L for each subcell using equation A.3.

For the 3J cell, since the bottom subcell clearly limits the current, the optimization is straightforward, being the only objective to reduce reflectance in the bottom subcell region in order to minimize the current mismatch. The calculated 3J bottom subcell J_L as a function of Si_3N_4 and SiO_2 thicknesses is presented in figure 3.16a. The initial EQE experimental measurement required as input was performed for a 3J cell that had already a 65 nm Si_3N_4 single-layer ARC and therefore, this layer was also included in the initial cell structure. Consequently, the minimum Si_3N_4 thickness is the 65 nm already deposited. Nonetheless, as shown by the simulation results, the highest bottom subcell J_L is obtained for a Si_3N_4

thickness of around 75 nm and therefore, reduction of initial Si_3N_4 thickness was not required.

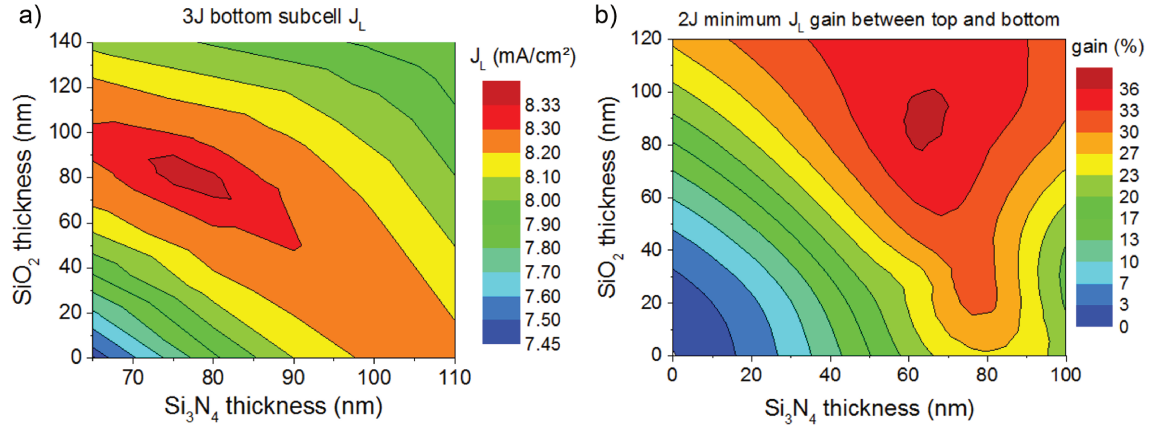


Fig. 3.16 Simulations as a function of Si_3N_4 and SiO_2 thicknesses for a) 3J bottom subcell J_L and b) minimum J_L gain between the 2J top and bottom subcells.

In the case of the 2J cell, since top and bottom subcells produce a similar photocurrent, reflectance has to be reduced in the full spectrum to maintain the subcell current match. For this reason, the optimization is based on both the top and bottom subcell photocurrents. Since the lowest subcell J_L limits the overall device current, the minimum J_L gain between the top and bottom is used for the optimization, as shown in figure 3.16b. Similar to the 3J, the experimental EQE input without ARC could not be measured and instead the EQE with a 65 nm Si_3N_4 single-layer ARC was used. Conversely, in this case, the Si_3N_4 layer was not included in the initial cell structure in order to allow reflectance simulations for Si_3N_4 thicknesses below 65 nm. However, this implies that the calculated EQE and J_L absolute values are not accurate and hence only relative values have to be considered.

The 3J simulations predict a bottom subcell J_L improvement of 11% by adding 85 nm of SiO_2 to the already present 65 nm of Si_3N_4 and was confirmed experimentally as shown in figure 3.17. This allows current mismatch reduction, but the bottom subcell still limits the current of the 3J cell. Reflectance in the bottom subcell absorption region is reduced from around 10-20% to only 5%. The simulated reflectance does not reproduce exactly the experimental results, probably due to cell layer thicknesses and doping level variation, which modify material optical properties and produce some incertitude into the calculation.

For the 2J simulations, the use of a double-layer 65 nm/85 nm $\text{Si}_3\text{N}_4/\text{SiO}_2$ ARC improves J_L by 36% compared to a cell without any ARC and by 13% compared to the 65 nm Si_3N_4 single-layer. In figure 3.18, the experimental EQE and R curves obtained for two different

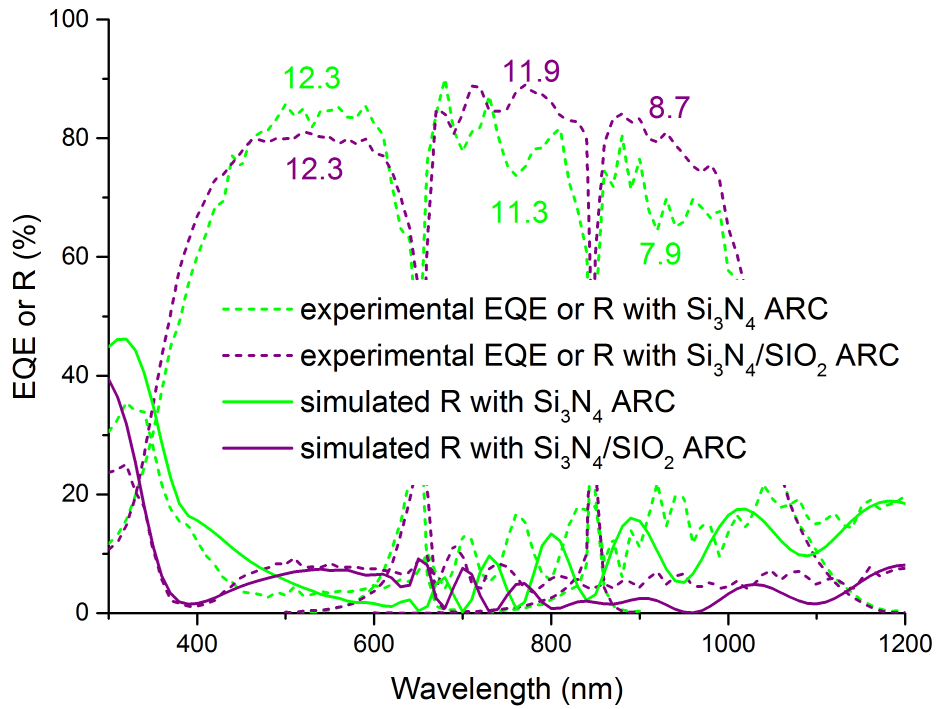


Fig. 3.17 Simulated and experimental Reflectance (R), together with the EQE of a 3J device with single Si_3N_4 and double-layer Si_3N_4/SiO_2 ARC. Subcell J_L in mA/cm^2 calculated with the AM1.5D spectrum are also included.

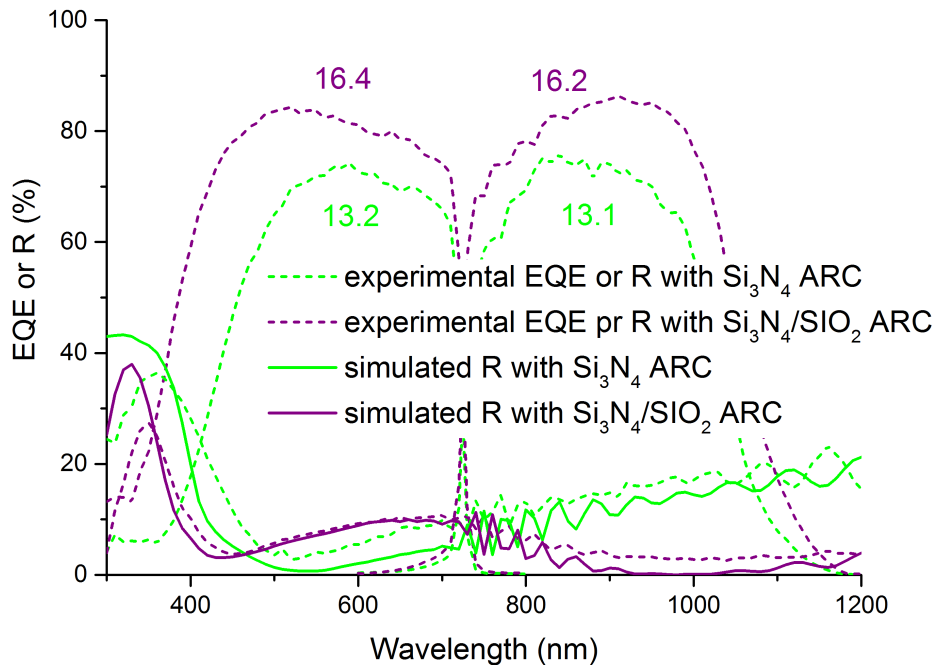


Fig. 3.18 Simulated and experimental Reflectance (R), together with the EQE of a 2J device with single Si_3N_4 and double-layer Si_3N_4/SiO_2 ARC. Subcell J_L in mA/cm^2 calculated with the AM1.5D spectrum are also included.

2J tandem cells are presented, one with 2J-A structure and single-layer ARC (Sample 2J-A, in green) and the other with 2J-B structure and double-layer ARC (Sample 2J-B, in purple). Similar to the 3J, the reflectance in the bottom subcell absorption region is reduced from around 10-20% to only 5%. In the top subcell, the reflectance is reduced from 300 to 500 nm, but then it increases from 500 to 720 nm. Contrary to the 3J, the observed improvement of EQE and J_L values cannot be attributed only to the double-layer ARC, because these cells have different designs in addition to different ARC layers.

3.5 Summary of fabricated tandem cells

In table 3.7, the summary of the different 2J and 3J tandem cells fabricated by SAB is presented, detailing its characteristics and different optimizations implemented. GaAs intermediate layers thickness is only indicated for the 2J because this is not detrimental for the 3J configuration. Si_3N_4/SiO_2 back surface passivation could only be tested in Si single-junction cells.

For the 2J, even if the Si bottom subcell EQE of Sample 2J-C was better than that of Sample 2J-B, the top subcell window showed degraded quantum efficiency, probably due to a growth issue, limiting the performance of the tandem. Nonetheless, record efficiencies were obtained for Sample 2J-B, as will be presented in the next chapter. For the 3J, Sample 3J-G is expected to be the most efficient, however $I-V$ characterizations could not be done yet and therefore Sample 3J-E is the one presented in chapter 4.

III-V structure	Sample name	GaAs thickness	Si substrate	Si fabrication process	Back surface passivation	CMP on Si side	ARC
2J-A	Sample 2J-A	225 nm	CZ	diffusion	BSF	yes	Si ₃ N ₄
2J-B	Sample 2J-B	85 nm	CZ	diffusion	BSF	yes	Si ₃ N ₄ /SiO ₂
2J-C	Sample 2J-C	40 nm	FZ	diffusion	BSF	yes	Si ₃ N ₄ /SiO ₂
3J Fraunhofer-ISE	Sample 3J-D	-	CZ	diffusion	BSF	yes	Si ₃ N ₄ /SiO ₂
3J Fraunhofer-ISE	Sample 3J-E	-	FZ	diffusion	BSF	yes	Si ₃ N ₄ /SiO ₂
3J Fraunhofer-ISE	Sample 3J-F	-	FZ	PIII	BSF	no	Si ₃ N ₄ /SiO ₂
3J Fraunhofer-ISE	Sample 3J-G	-	FZ	BLII	BSF	no	Si ₃ N ₄ /SiO ₂

Table 3.7 Summary of the different 2J and 3J tandem cells fabricated by SAB, detailing its characteristics and different optimizations implemented.

3.6 Conclusions

The design and independent fabrication of the III-V and Si subcells was presented in this chapter. The first part is dedicated to the AlGaAs top subcell design for the 2J tandem cell. The choice of an AlInP window and GaInP emitter, forming a n-GaInP/p-AlGaAs heterojunction, allowed to keep the 1.7 eV optimum top cell bandgap and led to a I_L top subcell improvement of 7.3%, thanks to the short wavelength enhanced performance. In addition, the increase in light transmission to the bottom subcell by reduction of GaAs bonding layer thickness and the use of a higher bandgap AlGaAs tunnel junction resulted in a bottom subcell I_L improvement of 6.8% respect with the first designs.

In the second part, the Si bottom subcell design was studied, specially for the 3J configuration, since in this case, current mismatching between the III-V and Si bottom subcells is high. PC1D simulations allowed to identify the key factors that limit the Si subcell performance, being the bulk lifetime the most critical characteristic that needs to be improved in our thick cells. In the case of III-V//Si interfaces with high FSRV, an emitter with a highly doped surface is crucial to achieve good surface passivation and to maximize V_{OC} , outweighing the drop in I_{SC} due to lifetime degradation. Back surface passivation is also important, specially to increase the infrared response.

Si bottom subcells were then fabricated using high quality FZ substrates. Different thermal diffusion or implantation processes for emitter and BSF formation were studied. Boron diffusion is detrimental for substrate lifetime, while implantation processes are more favorable in this respect, even if the doping profiles are deeper. In addition, smoother surfaces are produced, thus allowing bonding without CMP. However, the presence of iron metallic impurities, which are probably activated during high temperature steps, still limit the performance of the Si subcells.

The ARC was optimized by transfer-matrix simulation methods. Using a $\text{Si}_3\text{N}_4/\text{SiO}_2$ double-layer, instead of the initial Si_3N_4 single-layer, the reflectance in the bottom subcell absorption region was reduced from around 10-20% to only 5%, which allowed current mismatch reduction for the 3J cell.

The design and fabrication process optimization allowed to obtain record tandem cell efficiencies, which were measured using a new $I-V$ characterization method adapted for MJSC under low concentration, as will be presented in the next chapter.

Chapter 4

Light I – V characterization methods for multi-junction solar cells

Light I – V characterization methods for MJSC are described in this chapter. First, the objectives of the I – V characterization are introduced and the special requirements for MJSC accurate efficiency measurement are explained. Afterwards, different types of solar simulators and irradiance sensors are presented along with the known methods for solar simulator spectrum adjustment. Finally, a new method for the characterization of MJSC based on pseudo-isotypes is presented and it is applied to measure our 2J and 3J solar cells under low concentration, allowing us to obtain a record efficiency for the 2J 2T Si-based tandem solar cell.

4.1 Introduction and challenges

As we have seen in chapters 1 and 3, an accurate and fast I – V characterization method is essential for the development and optimization of MJSC. EQE and R measurements are not enough to assess critical parameters as the I_{SC} , V_{OC} , FF and η , or losses caused by R_s , that can only be obtained from the I – V curve under illumination.

Standard Reporting Conditions (SRC) are needed to enable comparisons between cells and measurements performed by different laboratories with different equipments. SRC are defined by an incident irradiance of 1 sun, $G^* = 1000 \text{ W m}^{-2}$, a precise spectral irradiance distribution or reference spectrum, G_λ^* [$\text{W m}^{-2} \text{ nm}^{-1}$], and a temperature of 25 °C. The reference spectrum for flat-plate (non-concentrating) PV is the global reference spectrum, AM1.5G, [238, 239, 25], while the direct reference spectrum, AM1.5D, is used in CPV [24, 240], which, as already seen in section 1.2.1, is similar to the AM1.5G spectrum except

for the lack of diffuse sky radiation. Even so, the integrated incident irradiance is still defined as 1 sun and thus, $G = X \cdot 1000 \text{ W m}^{-2}$, where X is the concentration factor.

The electrical conversion efficiency depends on temperature, light intensity and, specially in the case of MJSC, also on spectral irradiance. The spectral irradiance is critical for the correct measurement of MJSC efficiency and therefore, the incident spectrum should ideally be exactly the same as the reference spectrum. Nevertheless, in general neither the spectra produced by the Sun or solar simulators perfectly match the reference [241] and hence the incident spectrum has to be carefully measured and adjusted in order to evaluate and reduce the uncertainty.

Since single-junction solar cell efficiency depends in general only on temperature and light intensity, standardized accurate measurement procedures are commonly used. However, classical characterization methods and standards are insufficient for MJSC and therefore its accurate and fast measurement is still challenging, specially in a 2T configuration because in this case the subcells are interconnected in series by tunnel junctions and thus the electrical properties of the individual subcells cannot be measured separately. As a result, MJSC are much more sensitive to the incident spectral irradiance distribution, first because the solar spectrum is divided in several regions, each of them absorbed by only one subcell and second because the total device I_{SC} is generally limited by the least generating subcell, as already seen in section 1.2.5. Therefore, the spectral irradiance has a strong impact on the subcell photocurrent ratios and can even control which subcell limits the overall device current, resulting in a high I_{SC} uncertainty that strongly impacts the MJSC efficiency. The subcell photocurrent balance also affects significantly the FF of the device [242–249].

Besides, measurements at irradiance higher than 1 sun present additional challenges, such as heating, which complicates the temperature control or the measurement of total and spectral irradiance. For these reasons, different standards and procedures are needed for an accurate MJSC efficiency characterization.

4.1.1 Requirements for MJSC characterization

For an accurate MJSC I – V measurement under illumination, the solar simulator producing the incident spectrum has to be carefully adjusted in order to obtain the same photocurrent balance between the subcells as under reference conditions. For measurements under 1 sun, this means that each subcell has to produce the same photocurrent as under the reference spectrum [250, 251]. For measurements under concentrated light, this condition can be expressed as having the same concentration factor for every subcell [240].

The concentration factor of a subcell, $X_{\text{sub } i}$, is defined in equation 4.1 as the ratio between the measured I_{SC} under the solar simulator spectrum, $I_{\text{sub } i}^{\text{sim}}$, and the I_{SC} produced under the reference spectrum at 1 sun, $I_{\text{sub } i}^*$, i being the index of the subcell: top or bottom for a 2J solar cell and top, middle or bottom for a 3J solar cell.

$$X_{\text{sub } i} = \frac{I_{\text{sub } i}^{\text{sim}}}{I_{\text{sub } i}^*} \quad (4.1)$$

$$SMR(\text{sub } i/\text{sub } j) = \frac{X_{\text{sub } i}}{X_{\text{sub } j}} \quad (4.2)$$

As shown in equation 4.2, the spectral matching ratio, $SMR(\text{sub } i/\text{sub } j)$ [252], is defined as the ratio between the concentration factors of two different subcells i and j . The SMR is a measure of the error produced by the spectral mismatch between the solar simulator and the reference spectra for a specific pair of subcells. When $SMR(\text{sub } i/\text{sub } j) = 1$, the concentration in both subcells is the same and thus the solar simulator produces the same subcell photocurrent balance as the reference spectrum. On the contrary, if SMR differs from one, the concentration in each subcell is different. Taking a 2J as an example, if $SMR(\text{top}/\text{bottom}) > 1$, the top subcell is under higher concentration than the bottom and hence the spectrum is blue-rich with respect to the reference. Conversely, if $SMR(\text{top}/\text{bottom}) < 1$, the bottom subcell is under higher concentration than the top and thus the spectrum is red-rich with respect to the reference.

Therefore, the spectral irradiance measurement requirements for an accurate MJSC characterization can be defined as having a SMR close to unity, within a required tolerance, for each combination of subcells. As stated in the recent IEC 62670-3 standard [240], for subcell current mismatch below 25% under reference conditions, the SMR should be within 10% of unity. Equations 4.3 and 4.4 summarize these requirements for a 2J and a 3J respectively.

$$SMR(\text{top}/\text{bottom}) = 1.0 \pm 0.1 \quad (4.3)$$

$$SMR(\text{top}/\text{middle}) = SMR(\text{top}/\text{bottom}) = 1.0 \pm 0.1 \quad (4.4)$$

4.2 Types of light sources and solar simulators

Since the spectral irradiance distribution of outdoor natural sunlight varies widely with location, atmospheric conditions and time of day and year, the Sun cannot be directly used as a reference source. Therefore, solar simulators are used to produce artificial illumination that simulates natural sunlight for accurate solar cell characterization under repeatable test

conditions. A solar simulator usually includes a light source, an I – V curve tracer and means for evaluating the measurement conditions, i.e. irradiance and temperature.

Light sources typically used in solar simulators are either xenon arc (Xe-arc) lamps or tungsten halogen filament lamps [253]. Both types have advantages and disadvantages that can be evaluated in terms of stability and filtering requirements in order to match a reference spectrum, in which the color temperature and possible spectral lines play an important role. The color temperature of a light source is the temperature of an ideal black-body radiator whose spectral irradiance peaks at the same wavelength. The color temperature of the spectrum outside the atmosphere (AM0) is approximately 5800 K and peaks at 480 nm [23].

The color temperature of tungsten lamps is around 3400 K and peaks at 800 nm, thus the spectral irradiance distribution is shifted toward the longer wavelengths with respect to the Sun, producing an important energy deficit in the shorter wavelengths. Even though spectral matching can be improved by using dichroic filters, Xe-arc lamps are preferred because its color temperature is on the order of 5400 K, which is very close to that of the Sun. Tungsten lamps are however frequently used as complementary lights for multi-source solar simulators. In the case of Xe-arc lamps, Doppler-broadened Xe emission lines (or spikes) appear from 800 to 1000 nm and thus have to be filtered out in order to obtain a good spectral matching. The advantages of the filament lamp over the arc lamp are the intensity stability, which is maintained throughout the long life-time of the lamp. In contrast, arc lamps suffer from a chronic instability that slightly shifts the spectral irradiance from the UV toward the infrared and have a shorter lifetime [253].

Xe-arc lamps can be either steady-state, with continuous illumination; or pulsed, in which a short flash of some milliseconds is produced. Continuous lamps are commonly used for 1-sun characterization while pulsed lamps are more adapted for measurements under concentration because the short flash duration reduces heating and hence temperature control problems without the need for a shutter. However, the short pulse duration complicates the irradiance monitoring with a spectroradiometer. In addition, pulsed simulators may introduce transient artifacts [254–256], unlike continuous simulators which can usually assume that the device is in steady state. The light intensity, or concentration ratio, can be adjusted by changing the voltage at which the lamp flashes. However, by doing so, the temperature of the Xe plasma also changes causing the spectral irradiance to shift to higher or lower wavelengths. Other possibilities are changing the distance from the lamp to the test plane and using spectrally neutral filters or controllable apertures [257, 258].

Depending on the I – V measurement scheme, pulsed simulators can be either single-flash or multi-flash. In single-flash measurements the complete voltage sweep used to obtain the

I – V curve is performed during only one pulse. The pulse produced by these kind of lamps present a plateau of light intensity during which the irradiance should be ideally constant. However, significant spectral variation during the duration of the flash is common and thus detrimental for the accurate characterization of MJSC. This problem can be mitigated by reducing the portion of the flash during which the I – V curve is measured using a fast acquisition system [258]. On the contrary, in multi-flash measurements only one I – V pair is measured per pulse and hence there is no need for a plateau. The spectral variation during the pulse is used indeed to obtain different spectra that, depending on the time at which the I – V point is measured, range from more blue-rich at the beginning of the flash to more red-rich at the end when the plasma cools down [259, 252]. This technique to modify the spectral distribution does not require any additional elements to tune the spectrum and the energy required is much lower than that of a single-flash pulse because there is not a high intensity plateau [260]. An example of a multi-flash low-cost simulator is the Helios 3030 developed at IES-UPM and commercialized by Solar Added Value [261]. This simulator has been used for the characterization of 2J solar cells or more generally, 3J where one of the subcells is not current limiting, like 3J Ge-based solar cells in which the germanium bottom subcell delivers much more current than the top and middle.

Simulator architecture becomes more complex when more subcells are considered because a more precise adjustment of the spectrum is required. In general, the larger the number of subcells in the MJSC to be characterized, the larger the number of spectrally tunable elements that must be incorporated. The most complex single-source spectrally-variable simulators create different optical paths for each spectral band to independently adjust their intensity and spectrum. Total irradiance can be modified using adjustable apertures and attenuation filters while dielectric absorbers, optical filters and dichroic mirrors are used to adjust the spectral distribution. The different beams are finally combined and guided to the test plane by means of mirrors, beam splitters or fiber optics. Some examples of these approaches are the Terrestrial-High Intensity Pulsed Solar Simulator (T-HIPSS) [262, 249], used at NREL, or the X-Sim [263], used at Fraunhofer-ISE, which are single-source pulsed solar simulators that create 6 independent channels for measurements of MJSC with up to 6 subcells under concentration. A scheme is depicted in figure 4.1a.

Multi-source simulators use different lamps to allow further adjustment of the spectrum. The advantage of using different sources is that light can be added to any spectral band by simply increasing the lamp intensity, while single-source simulators can only remove parts of their light spectrum. However, the lamps must be well synchronized in time, which adds even more complexity and cost. For instance, a four-source pulsed simulator is used at Fraunhofer ISE for the characterization of MJSC under concentration [265] and at NREL the

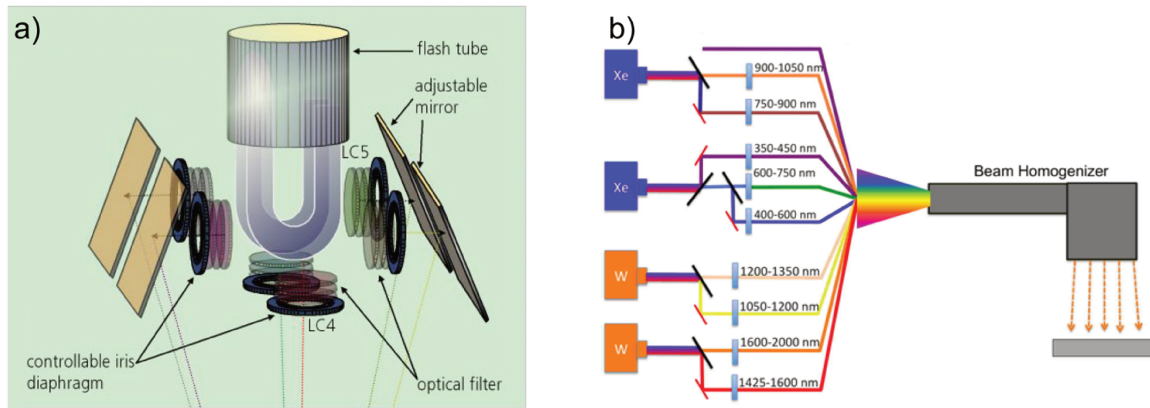


Fig. 4.1 a) X-Sim single-source pulsed solar simulator used at Fraunhofer-ISE with 6 independent channels for measurements of MJSC under concentration [263], b) One-Sun Multi-Source Simulator (OSMSS) used at NREL which combines 4 sources with optical fibers to create 9 independent channels [264].

One-Sun Multi-Source Simulator (OSMSS) combines 4 sources with optical fibers to create 9 independent channels [264]. A scheme is depicted in figure 4.1b. Since the use of different optical paths or multiple sources are often combined and both have similar characteristics in terms of complexity and cost, from now on multi-source solar simulators will designate both approaches.

4.2.1 Quality classification

The quality of solar simulators is typically classified according to three features: the spatial uniformity of the irradiance, the spectral matching to a reference spectrum and the temporal stability of the irradiance during a measurement [1, 266, 267]. Each characteristic can be classified in three different levels from A, the strictest requirements, to B or C, the most flexible requirements. Table 4.1 summarizes all the different specifications. However, these norms were conceived for standard solar simulators used to measure single-junction Si solar cells and hence do not directly apply for the specific requirements of MJSC or the use of concentrated light [260].

- **Spatial uniformity** of the light over the test area is required in order to reduce uncertainties in I_{SC} and concentration. As shown in equation 4.5, the spatial non-uniformity is calculated through the maximum and minimum light intensities found over the defined test area, which can be minimized by placing the irradiance sensor as close as possible to the device under test. As stated in the international IEC 60904-9 standard [1], class A is achieved if non-uniformity is below 2%. Besides, this non-uniformity

Class	Temporal instability	Spatial non-uniformity	Spectral match in bands
A	2%	2%	0.75 – 1.25 ($\pm 25\%$)
B	5%	5%	0.6 – 1.4 ($\pm 40\%$)
C	10%	10%	0.4 – 2.0

Table 4.1 Classification of solar simulators as stated in IEC 60904-9 [1]

can be a function of wavelength [248] and thus the uniformity of the spectral irradiance should be studied for every subcell spectral region.

$$\text{Spatial or temporal non-uniformity (\%)} = \left[\frac{G_{\max} - G_{\min}}{G_{\max} + G_{\min}} \right] \times 100\% \quad (4.5)$$

- **Temporal stability** of the irradiance during measurement is essential, specially for MJSC, in which a spectral variation can cause the limiting subcell to shift and hence produce artificial discontinuities in the I – V curve. For multi-flash measurements triggered by a light sensor, temporal stability depends on the maximum variation of irradiance that can be found between the detection of the reference level, at which the measurement is triggered, and the acquisition of the I – V curve. Therefore, it depends mainly on the sampling rate of the data acquisition system. Again, class A is achieved if the instability is not higher than 2% and can be calculated also with equation 4.5 in a similar way as the spatial uniformity.
- **Spectral matching** to the reference spectrum is the most critical characteristic for the accurate measurement of MJSC efficiency. Solar simulators used for the characterization of single-junction Si solar cells are spectrally classified by comparing the integrated irradiance found in different spectral bands of 100 or 200 nm with respect to the reference spectrum from 400 nm to 1100 nm [1]. Class A is achieved if the difference in irradiance is less than 25% in every spectral band. As already explained in section 4.1.1, the correct way to evaluate the solar simulator capability to obtain the same photocurrent balance between the subcells as under a reference spectrum is through the *SMR*. The widely used spectral quality classification using letters A, B or C cannot assure that the appropriate photocurrent balance is achieved and therefore significant measurement errors might be introduced even if a class A simulator is used [268, 269].

4.3 Validation of test conditions

In order to verify that the previously defined measurement requirements are met, cell temperature and irradiance have to be monitored during the I – V characterization.

4.3.1 Cell temperature

The efficiency of solar cells is dependent on temperature, with variations ranging from 0.1% to nearly 1% per degree Celsius depending on the structure and material [270, 271]. Measurement of cell temperature under concentrated light is problematic because large temperature gradients may exist between the measurement chuck and the cell junction or even within the cell itself. For this reason, no accepted method is available for directly measuring the temperature of cells operating under concentrated light. Nevertheless, the short flash duration of a pulsed solar simulator, of only some milliseconds, produces a small cell heating and therefore the cell temperature can be easily set before the flash [270, 272, 240]. As stated in IEC 62670-3 [240] the temperature shall be maintained at $25 \pm 2^\circ\text{C}$.

4.3.2 Spectral irradiance

As already explained in section 4.1.1, when MJSC are concerned, the irradiance must be evaluated for each subcell separately in order to verify that the incident spectrum produces the same subcell photocurrent balance as the reference, i.e. $SMR = 1.0 \pm 0.1$. There are two main approaches to verify this condition: the measurement of the simulator spectrum using a spectroradiometer and the use of spectrally matched reference cells, also known as component cells or “isotypes”.

4.3.2.1 Spectroradiometer

Spectroradiometers with array-detector monochromators are commonly used to measure the spectrum of solar simulators. A diffraction grating spatially separates the different wavelengths which are then projected into an array of Charge-Coupled Devices (CCD) or photodiode detectors. The greater the number of detectors, the larger the spectral range and/or spectral resolution. As before, new challenges arise for the measurement of spectra when MJSC and concentration measurements are considered. First, the wavelength range, defined by the spectral response of the device under test, is usually extended to about 1800 nm due to the use of small bandgap bottom subcell materials like germanium. Therefore, two different arrays are usually needed to cover the full spectrum. In addition, if pulsed solar simulators are used, very short integration times are required in order to be able to consider the spectrum

as constant during the measurement time, specially for multi-flash measurements without irradiance plateau. The shortest integration times of most detector arrays are in the range of 1 to 10 ms, which is too long for the correct measurement of the ever changing irradiance of multi-flash simulators [260]. An integration time on the order of 100 μ s would be needed in this case, but such short integration times are known to decrease the signal-to-noise ratio [273]. Non-linearity of detectors can also be a source of error for measurements under concentration because spectroradiometers are typically calibrated at low light intensities with a deficit of UV light [258].

An alternative to array-detectors are scanning monochromators. This kind of spectroradiometers does not attempt to measure the entire spectrum during a single flash and instead measures only a precise wavelength at a time. Therefore, several hundred of flash pulses are needed to cover the full wavelength range, which is very time consuming and relies on the repeatability between flashes [274].

4.3.2.2 Component “isotype” cells

Spectrally matched reference cells, component cells or isotypes are single-junction cells ideally having the same relative spectral response as each of the subcells composing a MJSC. They are used as sensors to estimate the photocurrent produced by each subcell under a solar simulator and, knowing their calibrated currents under 1-sun reference conditions, $I_{\text{ref } i}^*$, the subcell concentration levels can be also determined as shown in equation 4.6.

$$X_{\text{sub } i} \approx X_{\text{ref } i} = \frac{I_{\text{ref } i}^{\text{sim}}}{I_{\text{ref } i}^*} \quad (4.6)$$

Component cells are grown using the same stack of semiconductor materials as the MJSC to be tested, but with only one junction being an electrically active p-n diode. The rest of the layers in the epitaxial structure are electrically inactive p-p or n-n isotype junctions, which act as optical filters absorbing the same light wavelengths as their active counterparts in the MJSC. Therefore, only the photo-generated charge carriers produced in the electrically active p-n junction are collected and thus the spectral response should be in principle the same as the subcell in the MJSC. Indeed, carriers generated in the other isotype junctions are in general recombined before reaching the active junction. However, the recombination in high quality III-V materials is often radiative and hence the photons emitted this way by the upper junctions, with an energy equal to the bandgap, can be reabsorbed by the active junction underneath. In the case of MJSC this process is known as radiative coupling or luminescent coupling (LC) [275], whereas for single junctions is known as photon recycling

[276]. LC is non-linear and depends on illumination intensity and bias voltage, therefore its effect varies from component cells to actual subcells [277, 278]. In addition, photo-generated charge carriers produced in an electrically inactive layer could reach the active junction and be collected if the diffusion length is high and if they are produced close enough, for example in the buffer or bonding layer. For these reasons, obtaining exactly the same spectral response can be difficult [279] and therefore, spectrally matched component cells for new cell architectures are usually not available due to its complexity and cost.

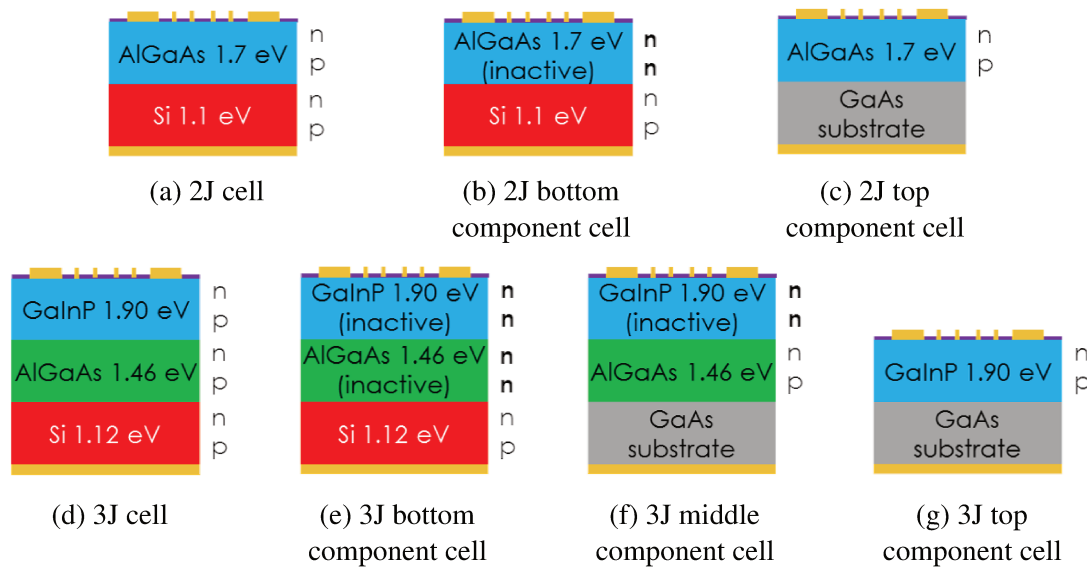


Fig. 4.2 Schemes of 2J and 3J component isotypes along with the respective tandem cells for comparison. The fabrication of the bottom isotype requires wafer bonding.

For example, in order to fabricate a set of component reference cells adapted for our 2J and 3J III-V on Si cell structures, which are schematized in figure 4.2, dedicated epitaxy and wafer bonding is required. For the bottom isotype of the 2J AlGaAs//Si cell, 4.2b, first an n-n isotype junction with the same layers and materials as the top subcell has to be grown, with the only difference being the doping, so that all layers are n-type. Then, the wafer bonding to the Si bottom subcell is done along with the rest of steps in the same way as for the tandem cell. The fabrication of a top reference cell is more simple because the top subcell is the only active junction needed and therefore the bonding process to a Si bottom subcell can be omitted. Moreover, an n-n isotype acting as spectral filter is not required and hence only a top junction of the same materials has to be grown as shown in figure 4.2c. However, by omitting the bonding process, the direction of growth is inverted with respect to the top junction in the tandem cell, which could create some differences due to the different order of layers during

epitaxial growth. In a similar way, the fabrication of a bottom component cell for the 3J design requires wafer bonding, while top and middle ones do not.

4.4 Methods for spectral irradiance adjustment

Different solar simulator architectures and spectral sensors are used for the measurement of MJSC. Spectral irradiance adjustment methods currently used in order to satisfy the $SMR = 1.0 \pm 0.1$ condition are either iterative and very time consuming (adaptation of the reference cell method to MJSC), are based on expensive multi-source solar simulators (linear equation system and R_{ij} methods) or rely on component cells having exactly the same spectral response as the one of the subcells (isotype method).

4.4.1 Reference cell method

Light I – V characterization of single-junction solar cells is commonly done using standard single-source solar simulators whose light intensity is measured using a calibrated reference cell. This method works well for single-junction devices because its I – V characteristic mostly depends on the temperature and total irradiance but not on the spectrum [280]. The relative spectral response of the reference cell is not required to be the same as the one of the device under test and therefore, given that even class A solar simulators do not perfectly match the reference spectrum, a spectral mismatch correction factor M , defined in equation 4.7, has to be applied. M takes into account the differences between the relative spectral response of the reference cell, SR_{ref} , and that of the device under test, SR_{DUT} , in relation to both the solar simulator, G_{λ}^{sim} , and the reference, G_{λ}^* , spectra [280–283].

$$M = \frac{\int_{\lambda} SR_{\text{ref}} \cdot G_{\lambda}^* d\lambda}{\int_{\lambda} SR_{\text{ref}} \cdot G_{\lambda}^{\text{sim}} d\lambda} \cdot \frac{\int_{\lambda} SR_{\text{DUT}} \cdot G_{\lambda}^{\text{sim}} d\lambda}{\int_{\lambda} SR_{\text{DUT}} \cdot G_{\lambda}^* d\lambda} \quad (4.7)$$

As in equation 4.7 any scaling factor cancels out, the reference cell method requires only the knowledge of the relative spectral distribution of the solar simulator and the relative spectral response of the device under test, thus eliminating the uncertainty in absolute measurements. In the case that absolute spectra and absolute spectral responses are used for the analysis, equation 4.7 can be interpreted as:

$$M = \frac{I_{\text{ref}}^*}{I_{\text{ref}}^{\text{sim}}} \cdot \frac{I_{\text{DUT}}^{\text{sim}}}{I_{\text{DUT}}^*} \quad (4.8)$$

The simulator intensity is then adjusted so that the current of the test cell under the solar simulator is the same as the one produced under the reference spectrum. When this is achieved, the second term of equation 4.8 cancels out and therefore equation 4.9 has to be satisfied, where $I_{\text{ref}}^{\text{sim}}$ is the directly measured reference cell current under the simulator and I_{ref}^* is the calibrated reference cell current under the reference spectrum.

$$I_{\text{ref}}^{\text{sim}} = \frac{I_{\text{ref}}^*}{M} \quad (4.9)$$

If the reference cell method is applied for the measurement of a MJSC using a spectrally variable single-source solar simulator, different spectral mismatch correction factors M_i have to be calculated for every subcell/reference cell pair as shown in equation 4.10.

$$M_i = \frac{\int_{\lambda} SR_{\text{ref } i} \cdot G_{\lambda}^* d\lambda}{\int_{\lambda} SR_{\text{ref } i} \cdot G_{\lambda}^{\text{sim}} d\lambda} \cdot \frac{\int_{\lambda} SR_{\text{sub } i} \cdot G_{\lambda}^{\text{sim}} d\lambda}{\int_{\lambda} SR_{\text{sub } i} \cdot G_{\lambda}^* d\lambda} \quad (4.10)$$

Similar as before, in order to obtain the same subcell photocurrents as under the reference spectrum, every reference cell current under the solar simulator must satisfy equation 4.11.

$$I_{\text{ref } i}^{\text{sim}} = \frac{I_{\text{ref } i}^*}{M_i} \quad (4.11)$$

However, in this case, in order to obtain the correct current values for all reference cells, the simulator spectral distribution has to be changed in addition to light intensity, but this modifies M_i and thus the simulator spectrum has to be measured again to re-calculate the new values. Therefore, an iterative procedure has to be applied, repeating the adjustment and measurement of the simulator spectrum until equation 4.11 is satisfied within a certain uncertainty for all junctions, which can be very time consuming [244, 284].

4.4.2 Linear equation system and R_{ij} methods

The linear equation system method is based on the use of a multi-source solar simulator with as many independent light sources as subcells. The spectrum of each light source must be adapted for each subcell spectral range of absorption and should not overlap with each other in order to easily adjust the current balance between them. Although in theory simple, such a multi-source solar simulator is in practice very complex to implement and usually expensive because it requires different lamps and/or optical systems to divide the light from one source into different spectral bands. The relative spectral irradiance of the different sources must be known, together with the subcell relative spectral response. Moreover, the light intensity

adjustment of the lamps has to be independent from their spectral distribution. When all these conditions are met, the solar simulator spectrum can be adjusted by solving a linear equation system where the solutions are the light intensity scaling factors of the different lamps [245]. Otherwise, the adjustment process also becomes iterative requiring the simulator spectrum to be measured at each time. Finally, a calibrated reference cell, which does not need to match the subcell spectral responses, is used to set the lamp light intensities using the calculated scaling factors. The R_{ij} method considers the more general case where the number of sources exceeds the number of subcells [264]. Although being a fast, accurate and highly adaptable method, developing complex multi-source solar simulators is expensive and hence often only possible for specialized characterization laboratories like NREL or Fraunhofer-ISE.

4.4.3 Isotype method

The isotype method uses a single-source multi-flash solar simulator coupled with spectrally matched component cells or isotypes [252, 259]. As already explained in section 4.2, spectral variation during the pulse is used to obtain different spectra without the need for additional tunable elements or different light sources. Due to the short duration of the flash and its continuous variation, both spectrally and in light intensity, the measurement of the simulator irradiance has to be done using isotypes ideally having exactly the same relative spectral response as the one of the subcells. Therefore, neither the spectral response nor the simulator spectrum measurements are in theory required. However, as already explained in section 4.3.2.2, fabricating an isotype cell with exactly the same spectral response can be difficult and in addition, any change in the tandem design can produce significant measurement errors if new perfectly matched isotypes are not used [285]. Consequently, since manufacturing new isotypes for every new cell architecture modification is expensive and time consuming [286], this reduces the adaptability of the method and its use for the development of new cell technologies.

4.5 Development of a new characterization method

The characterization methods that have been discussed till now could not be used at INES for the measurement of our III-V on Si cells. At INES, the only solar simulator adapted for MJSC characterization is a Helios 3030 with one multi-flash Xe lamp and therefore, the linear equation system or R_{ij} methods, which require an expensive multi-source solar simulator, cannot be applied. Due to the short duration of the flash pulse and the lack of an irradiance plateau, the simulator spectrum cannot be recorded using conventional spectroradiometers.

Characterization method	Spectral irradiance sensor	Solar simulator	+ Advantages – Disadvantages
Reference cell method [244]	reference cell spectroradiometer	single-source	+ low complexity/cost – time consuming (iterative)
Linear equation system [245]	reference cell spectroradiometer	multi-source	+ fast (non-iterative) – high complexity/cost
Isotype method [259]	isotypes	single-source multi-flash	+ low complexity/cost + fast (non-iterative) – lack of flexibility/accuracy
HCPI method (this work)	pseudo-isotypes spectroradiometer	single-source multi-flash	+ low complexity/cost + fast (non-iterative)

Table 4.2 Main characteristics of light I - V characterization methods for MJSC.

Therefore, the first option explored was the use of the isotype method in order to measure the subcell concentration ratios. However, spectrally matched component cells are difficult to manufacture and their spectral response do not perfectly match those of the subcells.

For these reasons, we developed a new characterization method combining the reference cell and the isotype methods. In this Hybrid Corrected Pseudo-Isotype (HCPI) method [287], instead of perfectly matched component cells, pseudo-isotypes formed by Si single-junction cells with optical filters are used, since they are easy to manufacture and adaptable to new cell designs by simply changing the filters. The use of a high-speed CMOS spectroradiometer, with a very short integration time of 100 μ s, enables the measurement of the multi-flash simulator spectrum and hence the calculation of M_i to correct the spectral mismatch. The spectrum adjustment is carried out using the pulse spectral variation during the lamp cool down and hence no additional tunable elements are needed, except AM1.5 or AM0 filters to reduce the Xe emission lines. The HCPI characterization method has the advantages of being fast, requiring only a low-cost single-source solar simulator and allowing the accurate efficiency measurement of new MJSC designs.

The previous characterization methods are summarized in table 4.2 and compared to the new developed HCPI method. As can be seen, the proposed HCPI method brings together the best of the reference cell and the isotype methods and eliminates their main disadvantages.

4.5.1 HCPI measurement principle

The I - V characterization by the HCPI procedure begins with the EQE measurement of the subcells and pseudo-isotypes. Then, the pseudo-isotypes are used to determine the time

during the flash decay at which $SMR(\text{ref } i / \text{ref } j) = 1$, defined as t^* . At a time $t' \simeq t^*$, the solar simulator spectrum is measured using the high-speed CMOS spectroradiometer. The I – V curves are then measured under different concentrations that are obtained by changing the distance between the lamp and the test plane. Finally, with the measured EQE and simulator spectrum, the M_i are calculated using equation 4.10 and the concentration ratios, previously approximated by equation 4.6, are corrected following equation 4.12 [260]. The SMR , defined in equation 4.2 can be then determined by equation 4.13.

$$X_{\text{sub } i} = X_{\text{ref } i} \cdot M_i \quad (4.12)$$

$$SMR(\text{sub } i / \text{sub } j) = SMR(\text{ref } i / \text{ref } j) \cdot \frac{M_i}{M_j} \quad (4.13)$$

4.5.2 Pseudo-isotypes

Instead of real n-n isotypes, which require a dedicated epitaxy and wafer bonding to the Si subcells, the HCPI method is based on the use of optical filters that are placed on top of Si single-junction cells, so that the absorption in the upper subcells is reproduced. The Si single-junction cells are easy to manufacture and inexpensive. In addition, they can adapt to different cell architectures by simply changing the filters. As an example, for our 2J design, a 720 nm long-pass filter (LPF720) is used in order to reproduce the absorption in the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ top subcell. In a similar way, the same Si cell can be also used as a bottom pseudo-isotype for the 3J design by using instead a 850 nm long-pass filter (LPF-850). Even if the manufacturing of top and middle component cells do not require wafer bonding, as already explained in section 4.3.2.2, the idea of using optical filters can also be applied. For the 2J and 3J top component cells, 720 and 850 nm short-pass filters (SPF-720 and SPF-850) can be used respectively, whereas the middle subcell of the 3J can be reproduced using a 650 nm long-pass filter (LPF-650) together with a 850 nm short-pass filter (SPF-850). In figure 4.3 schemes of the different pseudo-isotypes are depicted.

4.5.3 Helios 3030 multi-flash solar simulator

The light I – V characterization under concentration is performed using a Helios 3030 solar simulator developed at IES-UPM [261] and commercialized by Solar Added Value. This low-cost single-source simulator is based on a Xe multi-flash lamp that is placed on a motorized rail, as shown in figure 4.4, allowing to easily change the distance between the lamp and the measurement plane using a dedicated software. The combination of different distances and attenuation filters produces different concentration factors that can be modified independently from the spectral content. An AM1.5 filter is used to partially attenuate the Xe emission

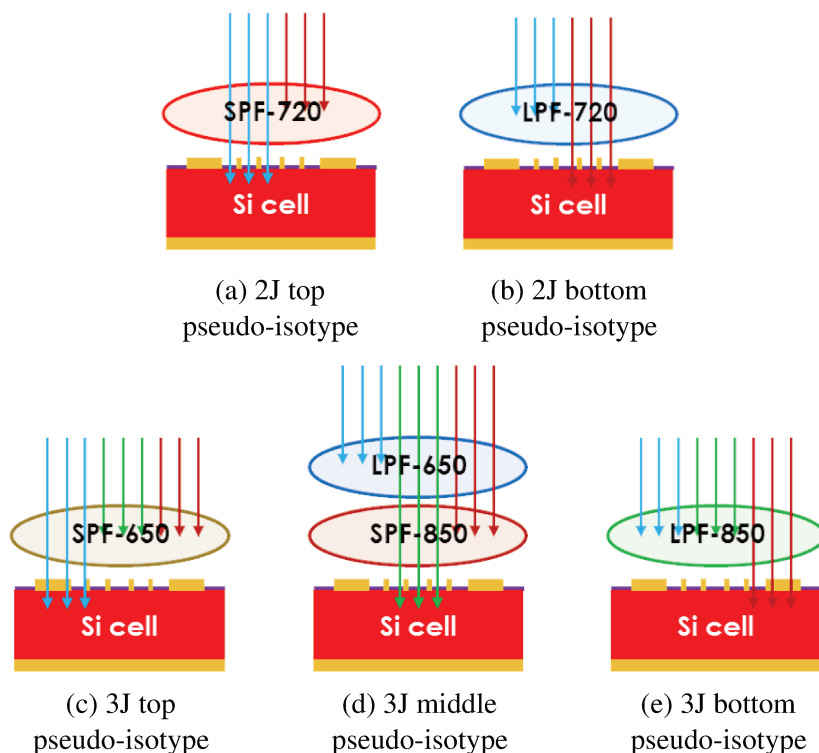


Fig. 4.3 Schemes of 2J and 3J pseudo-isotypes formed by a Si single-junction cell and optical filters placed on top.

lines, obtaining this way better spectral matching to the reference spectrum. The irradiance produced by the flash does not present a plateau and instead, as the lamp cools down after the flash peak, the irradiance starts to decrease while the spectral content changes continuously and smoothly from a blue-rich to a more red-rich spectrum. This is useful for tuning the spectrum because different spectral conditions are obtained depending on the time at which the I - V curve is measured. However, a multi-flash measurement is required in which every I - V pair point is measured within a different flash. About 20 flashes are needed in general to scan a complete I - V curve and thus high repeatability between flashes is needed.

The temperature is controlled using a Peltier thermoelectric plate where the device under test and component cells are placed. As shown in figure 4.4, the component cells are placed close to the device under test in order to reduce the errors related to spatial non-uniformity of the flash [248]. The non-uniformity in these conditions is found to be lower than 2%, which confers the class A classification as stated in the IEC 60904-9 standard [1]. Component cells are used to monitor the irradiance and the simulator spectrum during the decay of the flash, which allows to determine the precise moment when the $SMR(\text{ref } i / \text{ref } j) = 1$. Despite

the simple design and low cost of this equipment, it presents good flexibility by providing a wide variety of spectra that can be obtained independently from the concentration factor.

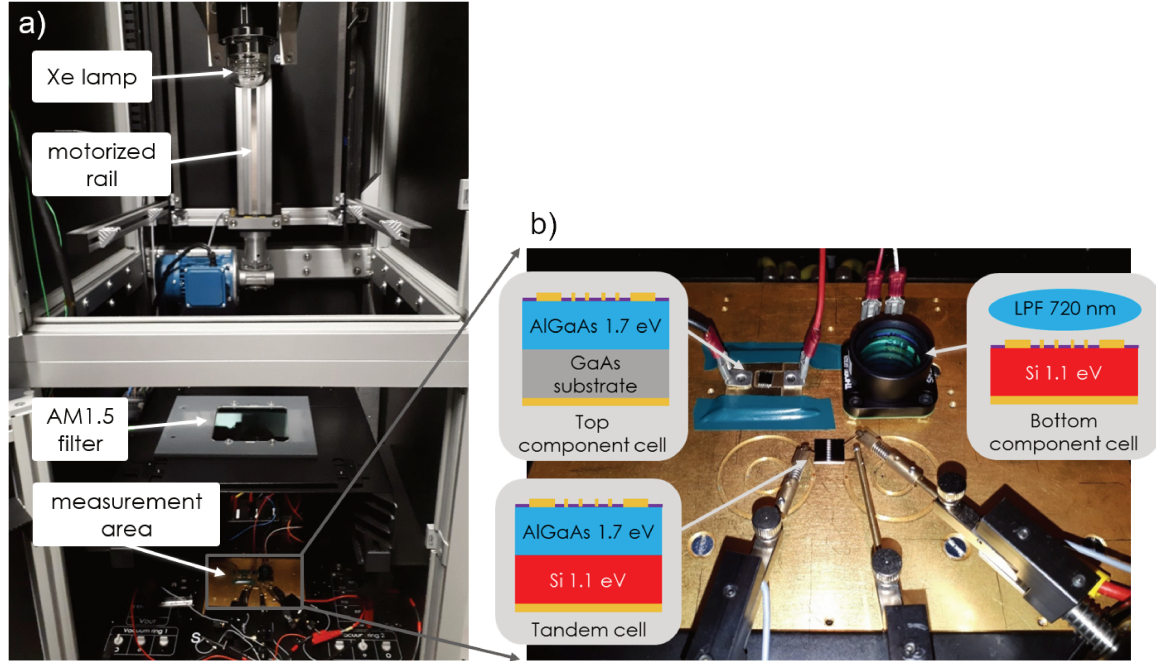


Fig. 4.4 a) Picture of the Helios 3030 single-source multi-flash solar simulator and b) measurement area where the component cells and device under test are placed.

4.5.4 CMOS spectroradiometer

The measurement of the multi-flash simulator spectrum is challenging due to the continuous irradiance and spectral distribution variation during the short duration of the pulse (~ 10 ms). To solve this problem the integration time, during which the entire spectrum is recorded, must be much smaller ($\sim 100\mu\text{s}$) so that the simulator irradiance can be considered as approximately constant. As explained in section 4.3.2, commonly used photodiode or CCD-array spectroradiometers have integration times in the range of 1 to 10 ms and those with shorter integration times suffer from a low signal-to-noise ratio and other electronic issues [273].

Only recently, commercially available spectroradiometers using arrays of Active-Pixel Sensors (APS) based on CMOS technology have shown good performance at such small integration times. APS are detectors having their own amplifiers and active noise canceling electronics. The AvaSpec-ULS2048CL-EVO (CMOS) spectroradiometer [288], used in this study, is based on this CMOS technology which combines the image sensor and

image processing functions within the same integrated circuit, allowing a good sensitivity and fast measurement. This CMOS spectroradiometer is formed by 2048 pixels, which provides a good spectral resolution, and includes a collection lens to enhance sensitivity in the 200–1100 nm. Its fast microprocessor and integrated electronics enable a minimum integration time of only 30 μ s, which is short enough to consider the simulator irradiance as approximately constant during the measurement time. This way, the simulator spectrum can be recorded at the time t' when the SMR measured by the pseudo-isotypes is close to 1.

4.6 2-Junction solar cell results

Sample 2J-B is characterized using the HCPI method described in the previous section. Their efficiency at 1 sun and under concentration is determined and the correct spectral conditions are assured through determination of the subcell concentration ratios, $X_{\text{sub } i}$, and their correction with M_i , which allows to verify the $SMR = 1.0 \pm 0.1$ condition.

4.6.1 EQE of subcells and component cells

A bottom pseudo-isotype formed by a Si single-junction cell and a LPF-720 placed on top is used as the bottom component cell as explained in section 4.5.2, figure 4.3b. The top component cell is an n-on-p $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ single-junction solar cell grown on a GaAs substrate with 2J-A structure, as reported in reference [127]. The differences with the top subcell of the 2J tandem cell (Sample 2J-B) are the materials used for the emitter ($\text{Al}_{0.2}\text{Ga}_{0.6}\text{As}$ instead of $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$) and the window layer ($\text{Ga}_{0.5}\text{In}_{0.5}\text{P}/\text{Al}_{0.6}\text{Ga}_{0.4}\text{As}$ instead of $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$) and the growth direction, which is inverted because wafer bonding was not performed in this case. Both the top AlGaAs component cell and the Si single-junction used for the bottom pseudo-isotype are covered with a SiN_x single layer ARC of 65 nm, as opposed to the $\text{SiN}_x/\text{SiO}_2$ (85 nm/85 nm) dual-layer of Sample 2J-B.

The EQE curves of the top and bottom component cells are compared in figure 4.5 with the results obtained for the top and bottom subcells of the tandem cell. As expected, the relative EQE of the component cells do not perfectly match the ones of the subcells. For the top component, the main reason is the different emitter material used, as shown by the EQE difference from 300 to 500 nm. In the bottom subcell, losses caused by parasitic absorption in the GaAs intermediate layers (tunnel junction and bonding layer) and recombination at the GaAs//Si bonding interface, already explained in section 3.2, do not appear in the bottom pseudo-isotype, as shown by the higher EQE values from 720 to 850 nm. In contrast, from 850 nm, the subcell EQE values are higher due to the improved dual-layer ARC design. In

order to evaluate whether if these component cells can be used to monitor the irradiance received by the subcells of the tandem cell and to correct the possible spectral mismatch, the M_i have to be calculated and hence the solar simulator spectral distribution is also needed.

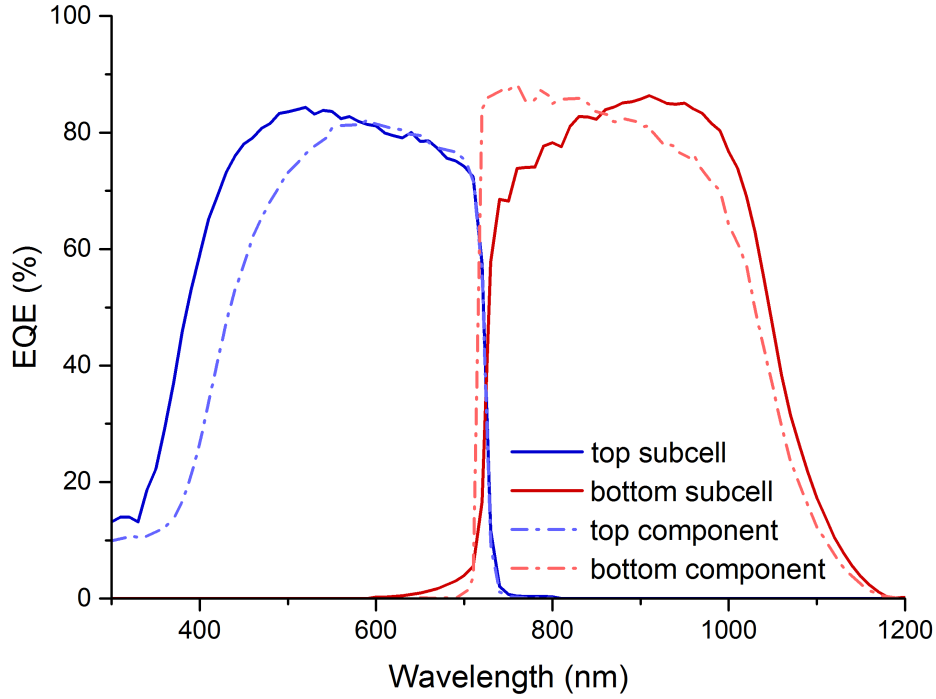


Fig. 4.5 EQE of the top and bottom 2J subcells along with the one of the component cells, which has been scaled for comparison.

For Sample 2J-B, the bottom subcell limits the overall current of the device under the AM1.5D reference spectrum, with a current mismatch of $CM^{(top/bottom)} = 1.02$. However, since the subcells are close to current-match, a small variation in the incident spectrum could change the current-limiting subcell.

4.6.2 Determination of $SMR = 1$ condition using component cells

As can be seen in figure 4.4b, the top and bottom component reference cells are placed near the device under test to monitor the solar simulator spectral irradiance during the decay of the flash. The measured currents of the component cells during the lamp discharge divided by their calibrated currents under reference conditions give the concentration factors, $X_{ref\ i}$, and with them, the $SMR^{(ref\ i/ref\ j)}$ can be calculated.

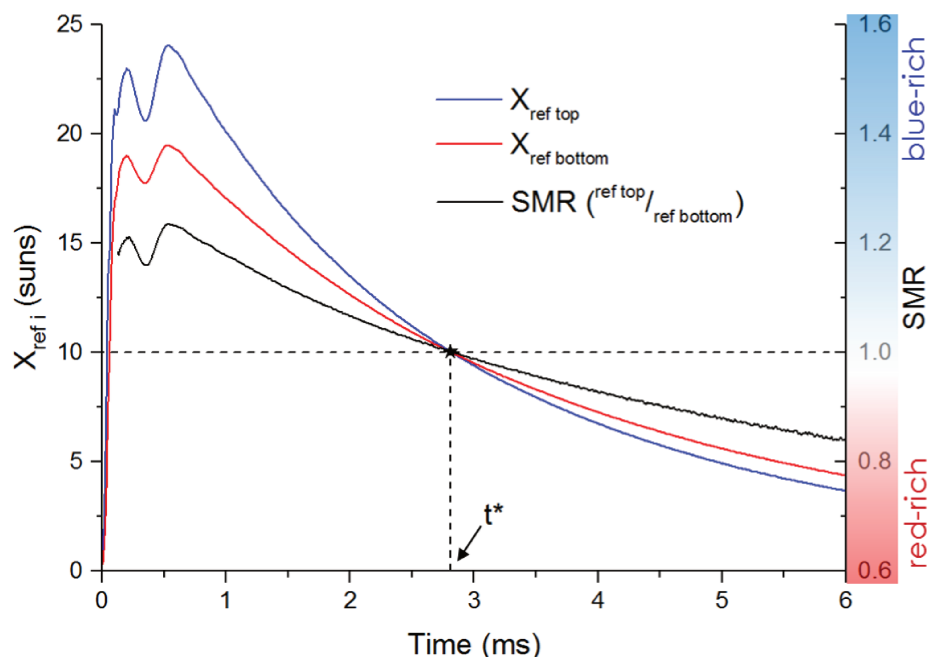


Fig. 4.6 Concentration factors measured by the top and bottom 2J component reference cells during the decay of the solar simulator flash along with the SMR . The distance between the lamp and the measurement plane is set empirically to obtain a concentration around 10 suns at $SMR = 1$.

As observed in figure 4.6, the irradiance produced by this kind of flash lamp does not present a plateau and instead an irradiance sweep with a different spectral top/bottom subcell balance is obtained. After the flash peak at around 0.5 ms, the lamp starts to cool down and hence the total irradiance decreases, as shown by the different variation in both $X_{ref\ top}$ (blue line) and $X_{ref\ bottom}$ (red line), starting at around 20-25 suns at the flash peak until about 5 suns at the end. The relationship between them, expressed by the SMR (black line), indicates the spectral variation. At the beginning, when the plasma temperature is higher, the simulator spectrum is more blue-rich than the reference spectrum: $X_{ref\ top} > X_{ref\ bottom}$ and hence $SMR > 1$. When the lamp temperature starts to decrease, the spectral content gradually turns into a more red-rich spectrum: $X_{ref\ top} < X_{ref\ bottom}$ and hence $SMR < 1$. Thanks to the smoothly change in spectral content, there is a precise instant at $t^* = 2.83$ ms, represented by a black star in figure 4.6, at which both component cells measure the same concentration factor, $X_{ref\ top} = X_{ref\ bottom} = 9.98$ suns, and thus $SMR(X_{ref\ top}/X_{ref\ bottom}) = 1$. In this example, the distance between the lamp and the measurement plane is set empirically in order to obtain a concentration close to 10 suns at $SMR = 1$.

The same is done with other lamp distances and attenuation mesh filters to obtain the $SMR = 1$ condition at different concentration ratios from 1 to 15 suns. Table 4.3 summarizes

X_{ref} (suns)	Lamp distance (m)	Filters
1	1.91	2 mesh filters + AM1.5
5	1.59	1 mesh filter + AM1.5
10	1.70	AM1.5
15	1.47	AM1.5

Table 4.3 Lamp distance and filters configuration to obtain $SMR = 1$ at different low concentration ratios.

the lamp distance and attenuation filters used in each case. As observed in figure 4.7, the time at which $SMR = 1$ condition is achieved slightly changes between the measurements at different concentrations. Although in theory changing the lamp distance and using spectrally neutral mesh filters to vary the concentration should not change the spectrum, this could accentuate the spatial non-uniformity of the incident light, explaining the small time differences detected by the component cells at which $SMR = 1$ condition is achieved. Ideally,

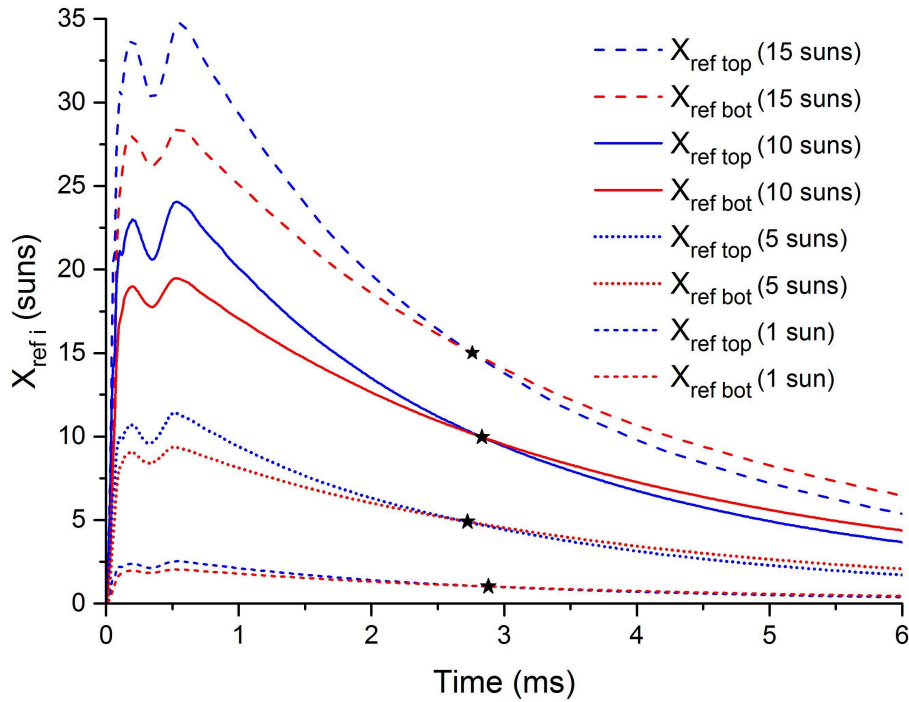


Fig. 4.7 Concentration factors measured by the top and bottom 2J component reference cells during the decay of the solar simulator flash with different distances between the lamp and the measurement plane and attenuation filters. The stars indicate the point at which $SMR(\text{ref top}/\text{ref bottom}) = 1$.

a measurement of the spectrum should be performed for all the different concentrations at the precise instant in which $SMR = 1$. Nonetheless, in order to simplify the characterization procedure, only one measurement of the spectrum is done at the time $t' = 3$ ms, which is justified because the SMR variation in such small time periods is less than 1%.

4.6.3 Flash spectrum measurement with CMOS spectroradiometer

The simulator spectrum, with and without an AM1.5 filter, measured at t' using the CMOS spectroradiometer, configured at an integration time of $50\ \mu\text{s}$, is shown in figure 4.8 along with the AM1.5D reference spectrum scaled to 10 suns for comparison. As can be seen, the use of an AM1.5 filter attenuates the Xe emission lines, obtaining this way a much greater resemblance to the AM1.5D reference spectrum. For the top subcell spectral region, from 300 to 720 nm, the resulting spectrum is quite similar to the reference. However, in the bottom subcell spectral region, from 720 to 1200 nm, some important differences are still present, for example due to the remaining Xe emission lines and atmospheric light absorption produced by O_2 and H_2O molecules.

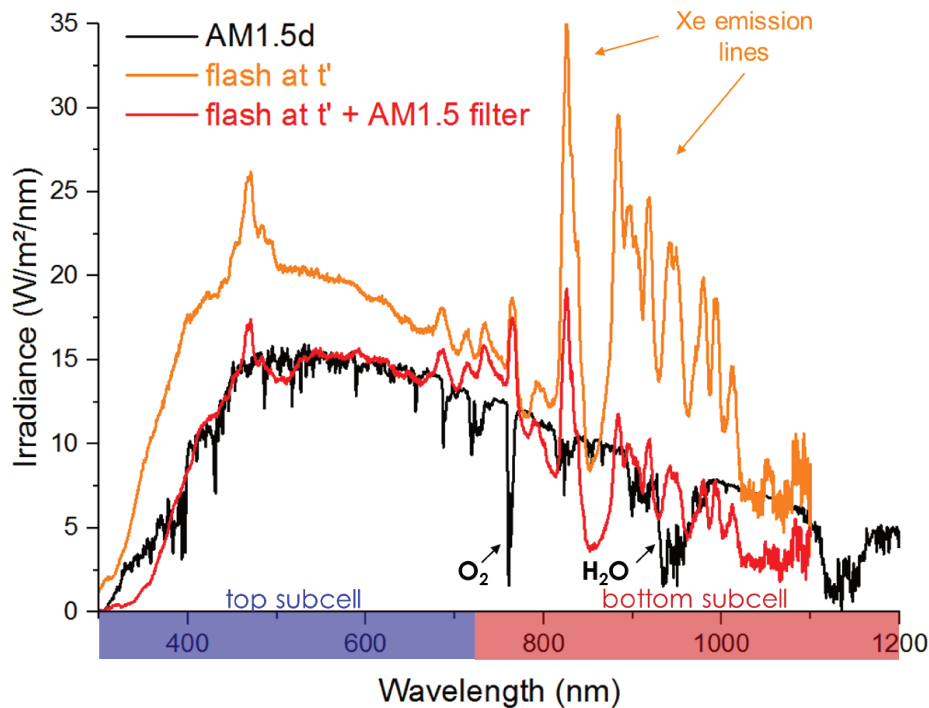


Fig. 4.8 Spectrum of the solar simulator flash measured at t' using the CMOS spectroradiometer with and without an AM1.5 filter along with the AM1.5D reference spectrum scaled to 10 suns for comparison.

4.6.4 Spectral mismatch correction factor

Knowing the spectral response of both the component cells and the subcells of the device under test, together with the spectral distribution of the solar simulator, allows to calculate the spectral mismatch correction factors M_i , following equation 4.10. M_i are useful to correct the errors in the concentration factors measured by the component cells due to the spectral mismatch. Since for the top subcell spectral region the simulator spectrum with the AM1.5 filter is very similar to the reference AM1.5D spectrum, the resulting $M_{\text{top}} = 0.999$ is very close to unity. However, since there are important differences in the bottom spectral region and the pseudo-isotype does not perfectly match the bottom subcell, the resulting $M_{\text{bottom}} = 0.968$ differs from unity by up to 3.2% and hence the $X_{\text{ref bottom}}$ measured by the pseudo-isotype has to be corrected following equation 4.12.

The effective *SMR* seen by the subcells of the tandem cell can be obtained with equation 4.13, which corrects the $SMR_{(\text{ref top}/\text{ref bottom})}$ measured by the isotypes. The resulting $SMR_{(\text{sub top}/\text{sub bottom})} = 1.03$ is slightly different from 1 but nonetheless, still within the 1.0 ± 0.1 range as required by the IEC standard [240]. As already shown in section 4.6.1, the bottom subcell is expected to limit the overall current of the tandem cell under the reference spectrum. Moreover, since the *SMR* is greater than one, i.e. the simulator spectrum is slightly more blue-rich compared to the AM1.5D reference spectrum, it is possible to confirm that the bottom subcell will also limit the overall current of the tandem during the I - V measurements and therefore the I_{SC} uncertainty will not be significantly affected by this small spectral mismatch.

4.6.5 I - V curves under low concentration

Due to the multi-flash nature of the solar simulator, each I - V curve is formed by around 20 (I , V) points, each one recorded during a different flash, at the same time instant and at a different applied bias voltage. The concentration measured by the component cells during each of the 17 flashes that are required to form the I - V curve under 10 suns is shown in figure 4.9. As can be seen, without taking into account the flash peak, the repeatability of the pulse during the lamp cool-down is very high, with *SMR* differences among flashes at the measurement time below 0.5%, which validates the repeatability of this multi-flash characterization method.

Since the bottom subcell limits the overall current of the tandem cell under the reference and simulator spectra, the tandem cell current is proportional to X_{bottom} and thereby it defines the total concentration of the device. For this reason, the bottom component cell is chosen as the irradiance reference cell and it is used to trigger the measurement of each (I , V) point.

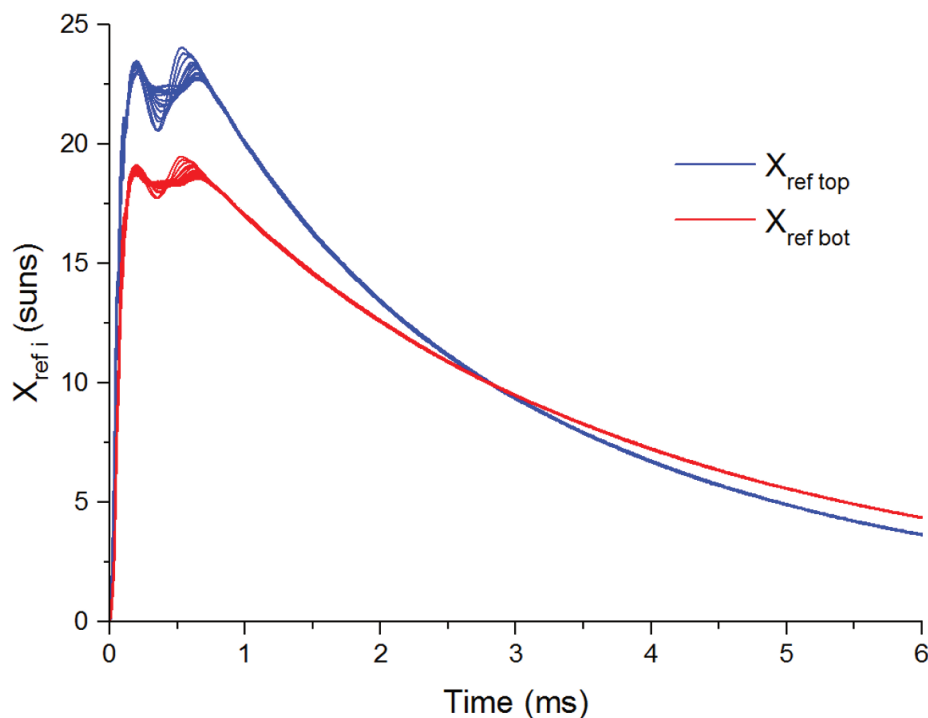


Fig. 4.9 Concentration measured by the 2J component cells during each of the 17 flashes that are required to form the I - V curve under 10 suns showing the excellent repeatability of the flash.

This way, when the bottom pseudo isotype measures the desired concentration level, the corresponding (I, V) values at such irradiance are recorded. The concentrations of 1, 5, 10 and 15 suns were selected before applying the correction with M_{bottom} and therefore the actual measurement conditions are different. The I - V curves measured under $SMR = 1.03$ are shown in figure 4.10 and the electric parameters extracted from them are listed on table 4.4.

As observed in figure 4.11, the J_{SC} is linear with concentration while the V_{OC} increases logarithmically, which agrees with the theory already explained in section 1.2.6. FF starts to decrease at 5 suns due to series resistance, which can be calculated from the I - V curves at different concentrations using the Swanson method [289–291], resulting in a $R_S = 0.35 \Omega\text{cm}^2$. This is close to the maximum series resistance of $0.3 \Omega\text{cm}^2$ estimated in section 2.3, allowing high FF values over 80% thanks to the oxide-free n^+ -GaAs/ n^+ -Si bonding interface enabled by SAB and the front metal grid design, which is adapted for these low concentrations. Efficiency at 0.97 suns is $21.1 \pm 1.5\%$ and it peaks as expected at around 10 suns due to the increase in V_{OC} , providing a record value of $23.7 \pm 1.7\%$ at 9.68 suns.

The results obtained are compared in table 4.5 with other confirmed Si-based tandem solar cell efficiencies from the literature. Although better efficiencies have been recently

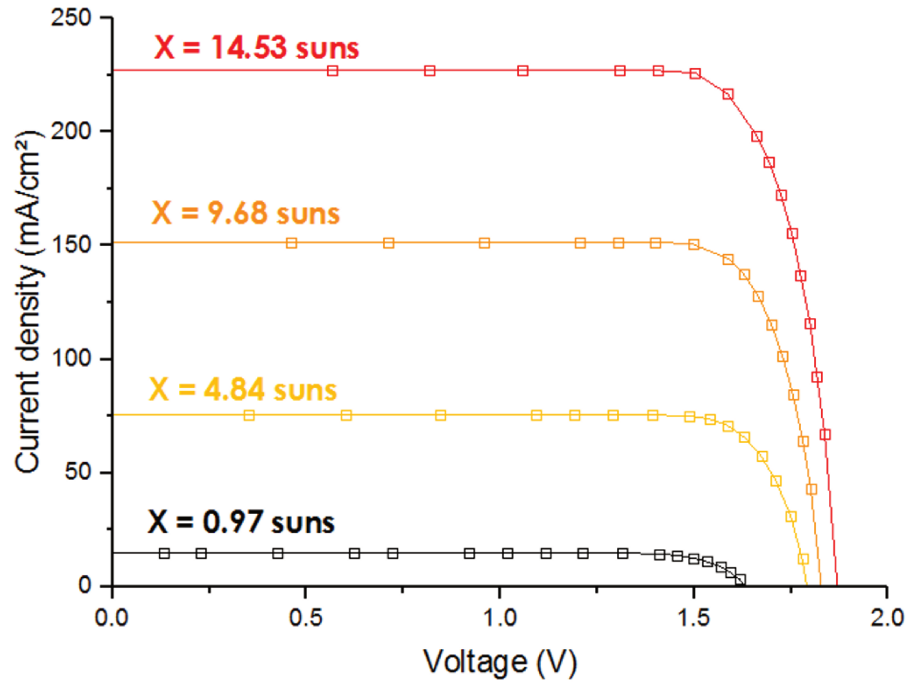


Fig. 4.10 I – V curves of 2J tandem cells under concentration factors from 1 to 15 suns

$X_{\text{sub top}}$ $\pm 3\%$	$X_{\text{sub bottom}}$ $\pm 3\%$	J_{SC} (mA/cm ²) $\pm 2\%$	V_{OC} (V) $\pm 1\%$	FF (%) $\pm 1\%$	η (%) $\pm 7\%$
14.99	14.53	227.40	1.87	80.7	23.6
10.00	9.68	151.63	1.83	82.6	23.7
5.00	4.84	75.81	1.79	83.6	23.4
1.00	0.97	15.16	1.63	82.5	21.1

Table 4.4 Concentration factors measured by the component cells and corrected with M_i , which gives the best estimation of the actual concentration seen by the subcells of the tandem cell. The 2J solar cell electric parameters obtained from the I – V curves at these concentration ratios are also included. Measurement uncertainties are expressed in relative values.

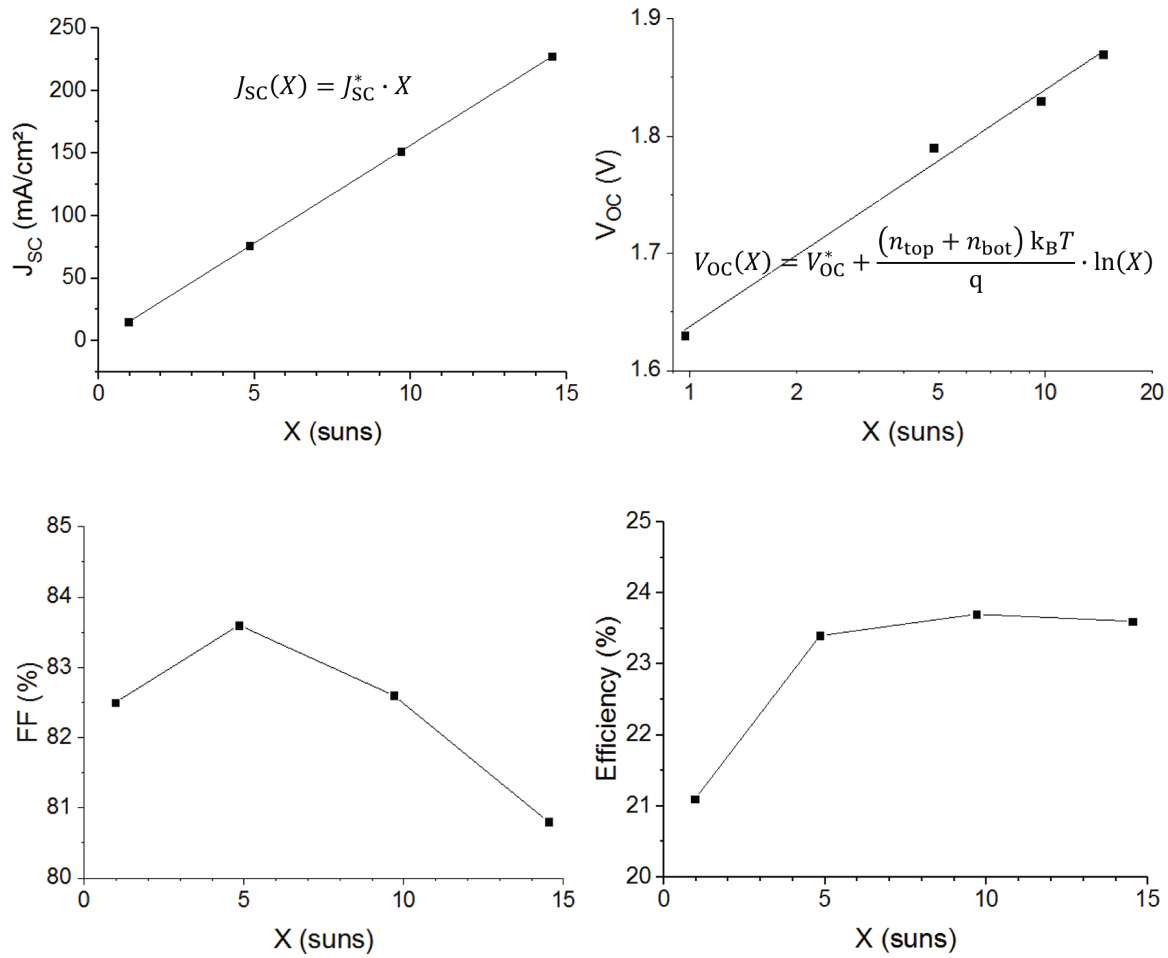


Fig. 4.11 2J electrical parameters extracted from the I - V curves as a function of concentration. J_{sc} increases linearly and V_{oc} as a logarithmic function. FF starts to decrease at 5 suns due to series resistance and the efficiency peaks at 10 suns due to the increase in V_{oc}

reported using three junctions or four terminals, these devices reach the highest efficiency to date for a 2J 2T Si-based tandem solar cell under low concentration, just above the best 2T 2J perovskite/Si cell achieved so far [292]. The efficiency under 1 sun is also the highest for a 2J 2T III-V on Si tandem solar cell. The uncertainty of the measurements using the HCPI method are higher partially due to the use of concentrated light and the corresponding higher complexity. However, since the method uses a single-source low-cost solar simulator, this higher uncertainty can be justified. In addition, the measurement of 4T devices is inherently more accurate because it is possible to independently obtain the electrical parameters of each subcell.

Materials	Configuration	η (%)	X (suns)	Institute
3J GaInP/GaAs//Si	4T mech. stack	35.9 ± 0.5	1	NREL/CSEM [48]
3J GaInP/GaAs//Si	2T wafer bonded	33.3 ± 1.2	1	Fraunhofer-ISE [79]
2J GaInP//Si	4T mech. stack	32.8 ± 0.5	1	NREL/CSEM [48]
3J GaInP/AlGaAs//Si	2T wafer bonded	25.2 ± 1.8	15	CEA (this work)
2J AlGaAs//Si	2T wafer bonded	23.7 ± 1.7	10	CEA (this work)
2J perovskite/Si	2T monolithic	23.6 ± 0.6	1	Stanford/ASU [292]
2J AlGaAs//Si	2T wafer bonded	21.1 ± 1.5	1	CEA (this work)
3J GaInP/GaAs/Si	2T monolithic	19.7 ± 0.7	1	Fraunhofer-ISE [34]

Table 4.5 Si-based tandem solar cell confirmed efficiencies reported in the literature compared to the results obtained in this work.

4.7 3-Junction Solar Cell Results

3J GaInP/AlGaAs//Si solar cells (Sample 3J-E) are also characterized using the HCPI method in a similar way as in the 2J case explained in the previous section.

4.7.1 EQE of subcells and component cells

Both middle and bottom pseudo-isotypes are used for the 3J cell. The middle is formed by a a LPF-650 and a SPF-850 placed on top of a Si single-junction cell, as shown in figure 4.3d, while for the bottom a LPF-850 is used, figure 4.3e. As can be observed in figure 4.12, the pseudo-isotypes approximately reproduce the bandgap and absorption range of the subcells. The top component cell is a GaInP single-junction cell, similar to the one shown in figure 4.2g, but with a bandgap of 1.81 eV, which does not exactly correspond to the 1.89 eV top subcell bandgap of our 3J cell.

The bottom subcell limits the whole photocurrent delivered by the 3J device under the AM1.5D reference spectrum, with current mismatches of $CM^{(\text{top}/\text{bottom})} = 1.25$ and $CM^{(\text{middle}/\text{bottom})} = 1.14$. Since the current mismatch is high, with a 25% current difference between top and bottom, the bottom subcell will limit the current even under small deviations from the ideal $SMR = 1$ spectral condition.

4.7.2 Determination of $SMR = 1$ condition using component cells

Similar to the 2J measurement, the top, middle and bottom component reference cells are placed near the device under test to monitor the solar simulator spectral irradiance during the

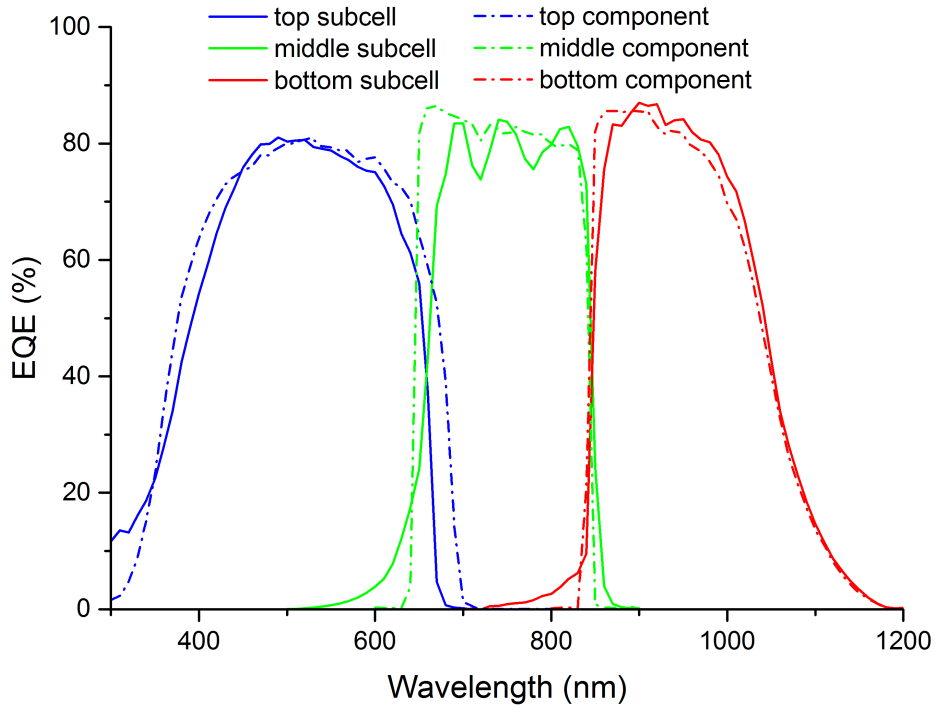


Fig. 4.12 EQE of the 3J subcells along with the one of the component cells, which has been scaled for comparison.

decay of the flash. For a 3J cell, the spectral irradiance of the flash can be then characterized by $X_{\text{ref top}}$, $X_{\text{ref middle}}$ and $X_{\text{ref bottom}}$, which can be used to calculate $SMR^{(\text{ref top}/\text{ref bottom})}$, $SMR^{(\text{ref top}/\text{ref middle})}$ and $SMR^{(\text{ref middle}/\text{ref bottom})}$.

First, as in the 2J measurements, the concentrations are recorded with the AM1.5 filter installed on the solar simulator. However, as can be observed in figure 4.13a, $SMR = 1$ condition for all junctions is impossible to achieve for the 3J cell under this configuration because there is not a precise instant in which all three component cells receive the same concentration factor. Instead, at the time when top and bottom reach $SMR^{(\text{ref top}/\text{ref bottom})} = 1$ condition, the middle component cell receives around 20% more irradiance, i.e. $SMR^{(\text{ref middle}/\text{ref bottom})} = 1.20$, exceeding the acceptable 10% spectral deviation from the reference spectrum, as stated by the IEC 62670-3 standard [240], which was already introduced in equation 4.4. Even if the bottom subcell could still be the current limiting subcell with this spectral conditions, in the same way as under the AM1.5D reference spectrum, such a high excess in current produced by the middle subcell can have a great impact on the FF .

Therefore, the flash spectral content has to be modified in order to obtain a spectrum with which the $SMR = 1.0 \pm 0.1$ spectral condition can be obtained for the three component cells. The AM1.5 filter was then replaced by an AM0 filter and the component cell concentrations

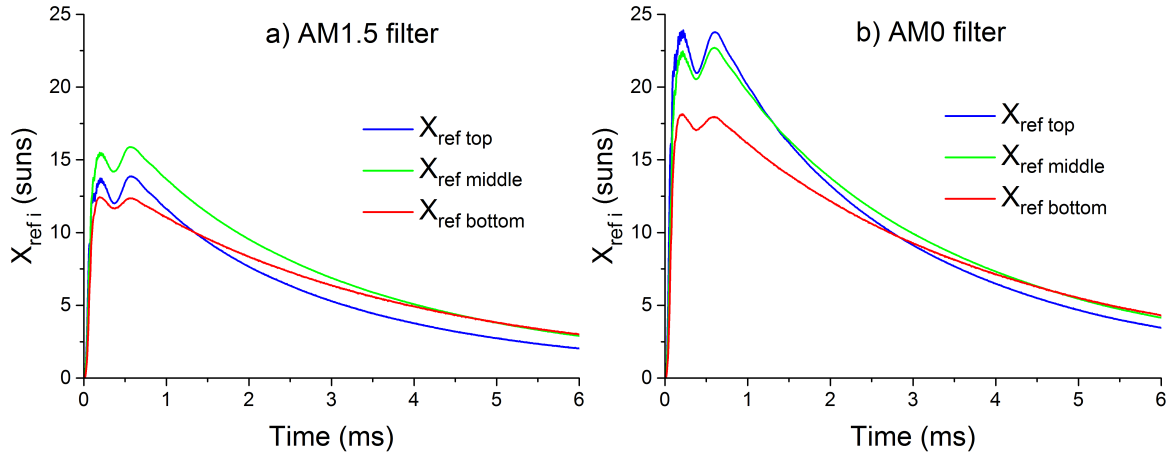


Fig. 4.13 Concentration factors measured by the top, middle and bottom 3J component reference cells during the decay of the solar simulator flash with either: a) the AM1.5 or b) the AM0 filter installed. The distance between the lamp and the measurement plane is set empirically to obtain a concentration around 10 suns at $SMR^{(ref\ top/ref\ bottom)} = 1$

were recorded again, as shown in figure 4.13b. With this configuration, it was found that at a time close to 3 ms, with top and bottom at $SMR = 1$, the relative middle component cell irradiance is only 8% higher, complying with the IEC 62670-3 standard. It should be noted that the use of an AM0 filter does not imply that the resulting spectrum is the AM0 reference spectrum, or even close. In fact, since the flash spectrum obtained with the AM0 filter produces the $SMR = 1.0 \pm 0.1$ condition using the 3J component cells, which are calibrated with the AM1.5D spectrum, it can be considered as an effective AM1.5D spectrum for this particular 3J cell technology.

4.7.3 Flash spectrum measurement with CMOS spectroradiometer

The simulator spectrum measured at 3 ms, with either an AM1.5 or an AM0 filter and with the CMOS spectrometer configured at an integration time of 100 μ s, is shown in figure 4.14. As can be observed, the flash with the AM0 filter has a higher blue content, which increases the photo-generated current in the top subcell. Incidentally, this is the reason why at 3 ms the spectrum complies with the $SMR = 1.0 \pm 0.1$ condition for the three component cells.

4.7.4 Spectral mismatch correction factor

The spectral mismatch correction factors M_i , are calculated with equation 4.10. The values obtained are $M_{top} = 1.005$, $M_{middle} = 0.993$ and $M_{bottom} = 1.022$. M_{top} and M_{middle} are very close to unity, while M_{bottom} differs by 2.2%. The spectral mismatch error in the concentra-

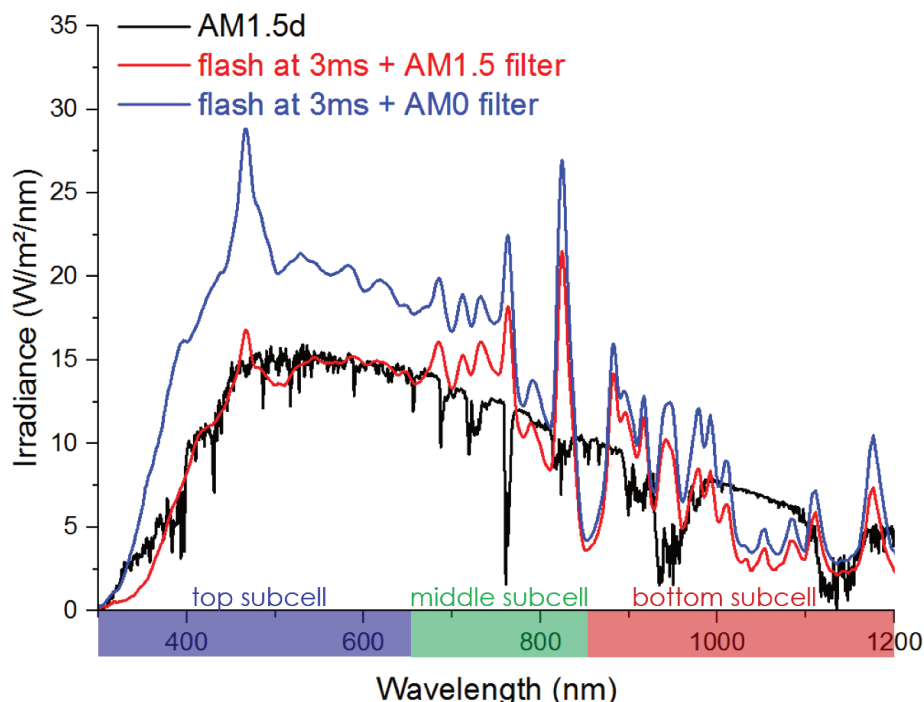


Fig. 4.14 Spectrum of the solar simulator flash measured at 3 ms using the CMOS spectroradiometer with either an AM1.5 or an AM0 filter along with the AM1.5D reference spectrum scaled to 10 suns for comparison.

tion factors measured with the 3J component cells are then corrected using equation 4.12, while equation 4.13 is used to correct the SMR . The resulting effective SMR seen by the subcells of the 3J cell are $SMR_{(sub\ top/sub\ bottom)} = 0.98$, $SMR_{(sub\ top/sub\ middle)} = 0.94$ and $SMR_{(sub\ middle/sub\ bottom)} = 1.05$. These values are slightly different from one but nonetheless still within the 1.0 ± 0.1 range as required by the IEC standard [240].

As already shown in section 4.7.1, the bottom subcell is expected to limit the overall current of the tandem cell under the reference spectrum, with the top subcell producing 25% more current ($CM_{(top/bottom)} = 1.25$). Therefore, even though the effective spectrum seen by the subcells produces a slightly more current in the top compared to the bottom subcell ($SMR_{(sub\ top/sub\ bottom)} < 1$), this spectral variation is not enough to change the current limiting subcell and hence the bottom subcell will also limit the overall current of the 3J cell during the I - V measurements. This way, the I_{SC} uncertainty will not be significantly affected by this small spectral mismatch.

4.7.5 I – V curves under low concentration

Since the bottom subcell limits the overall current under the reference and simulator spectra, X_{bottom} defines also in the 3J case the total concentration of the device. Therefore, the bottom component cell is chosen as the irradiance reference cell to trigger the measurement of each (I, V) point, in the same way as for the 2J measurements. The I – V curves measured under different concentration factors and at the *SMR* spectral conditions specified in the previous section are shown in figure 4.15. The electric parameters extracted from them are listed on table 4.6.

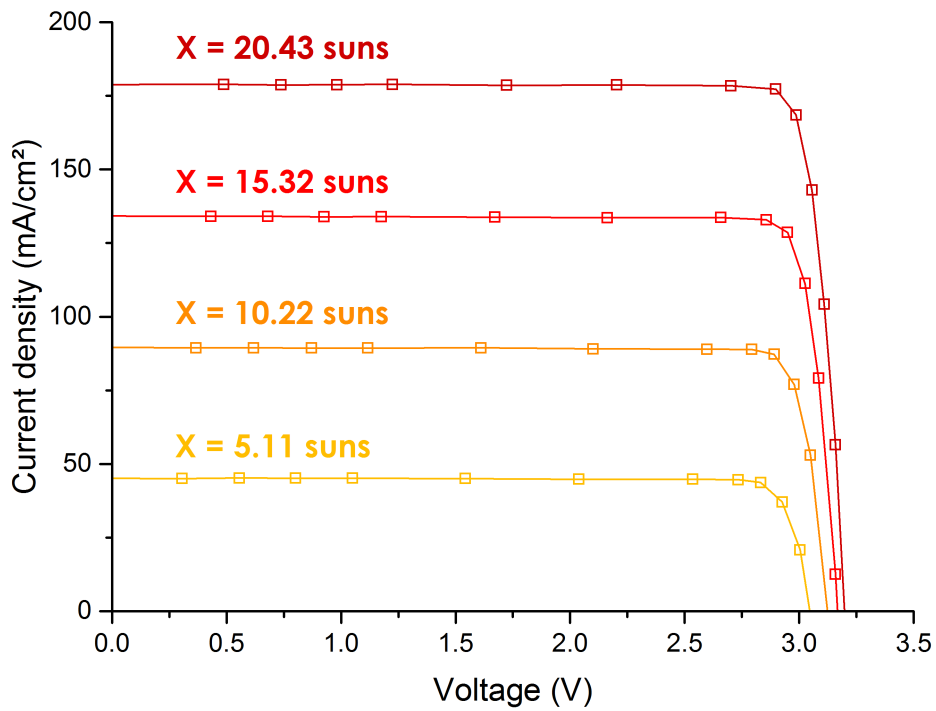


Fig. 4.15 3J cell I – V curves under concentration factors from 5 to 20 suns

The electrical parameters extracted from the I – V curves as a function of concentration are presented in figure 4.16. Similar to the 2J, the FF starts to decrease at 10 suns due to series resistance, $R_S = 0.38 \Omega \text{cm}^2$, calculated in the same way with the Swanson method [289–291]. The FF obtained, with values up to 90%, is higher than that of the 2J due to the higher V_{OC} of the 3J and higher current mismatch between the subcells. The efficiency peaks at around 15 suns with a value of $25.2 \pm 1.8\%$. As seen in table 4.5, these 3J cells are less efficient than the record 3J cells with a Si bottom subcell reported in the literature [79], with efficiencies as high as 33.3% at 1 sun for an equivalent technology. As already explained in chapter 3, the bottom subcell is the limiting factor of this 3J structure, because it suffers from high bulk and surface recombination.

$X_{\text{sub top}}$ $\pm 3\%$	$X_{\text{sub middle}}$ $\pm 3\%$	$X_{\text{sub bottom}}$ $\pm 3\%$	J_{SC} (mA/cm ²) $\pm 2\%$	V_{OC} (V) $\pm 1\%$	FF (%) $\pm 1\%$	η (%) $\pm 7\%$
5.02	5.36	5.11	45.20	3.05	89.8	24.2
10.05	10.73	10.22	90.39	3.12	90.2	24.9
15.07	16.09	15.32	135.60	3.17	89.9	25.2
20.09	21.46	20.43	180.79	3.20	88.6	25.1

Table 4.6 Concentration factors measured by the component cells and corrected with M_i , which gives the best estimation of the actual concentration seen by the subcells of the 3J cell. The solar cell electric parameters obtained from the I - V curves at these concentration ratios are also included. Measurement uncertainties are expressed in relative values.

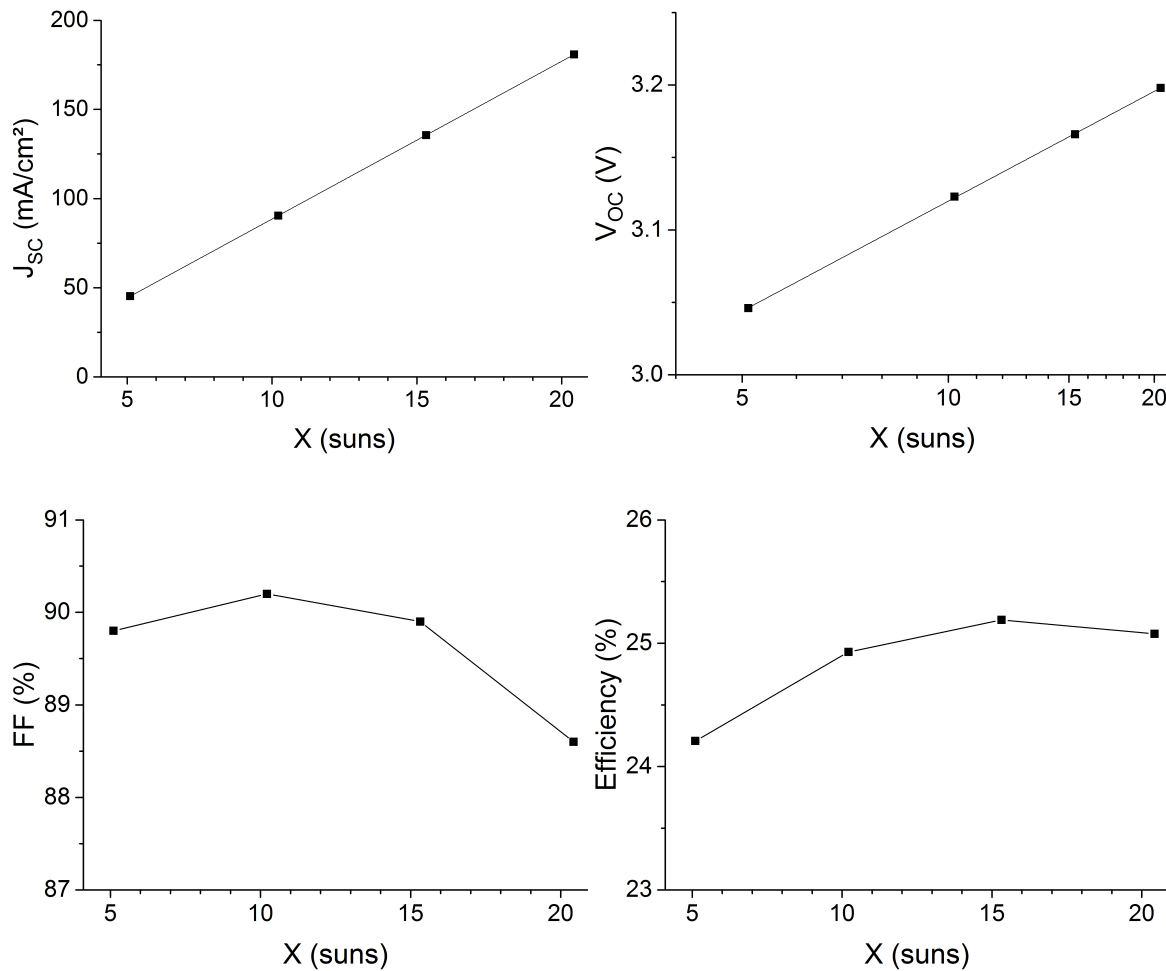


Fig. 4.16 3J electrical parameters extracted from the I - V curves as a function of concentration. J_{SC} increases linearly and V_{OC} as a logarithmic function. FF starts to decrease at 10 suns due to series resistance and the efficiency peaks at 15 suns due to the increase in V_{OC}

4.8 Conclusions

In conclusion, the so-called HCPI characterization method that has been developed during this PhD thesis is used for the evaluation of 2J and 3J cells. It is shown as a fast, low cost and easily adaptable technique for the development of new MJSC technologies because it does not require perfectly matched component cells. Instead, Si single-junction cells with optical filters are used as pseudo-isotypes and the measured X_i are corrected with M_i , which are calculated from the simulator spectrum and EQE measurements. The use of a high-speed CMOS spectroradiometer enables the measurement of the multi-flash simulator spectrum and hence the calculation of M_i to correct the spectral mismatch. The spectrum adjustment is carried out using the pulse spectral variation during the lamp cool down and hence no additional tunable elements are needed, except AM1.5 or AM0 filters to reduce the Xe emission lines.

The HCPI method has been applied for the characterization of 2J and 3J 2T III-V on Si tandem solar cells, obtaining the I - V characteristics under low concentrations. M_{bottom} differed from unity by up to 3.2% for the 2J cell and by 2.2% for the 3J cell, showing the importance of properly applying this spectral correction which directly affects the concentration and hence the measured efficiency. The relatively low series resistance, $R_S = 0.35 \Omega\text{cm}^2$ for the 2J and $R_S = 0.38 \Omega\text{cm}^2$ for the 3J, enabled high FF values, over 80% for the 2J and up to 90% for the 3J, thanks to the highly conductive n^+ -GaAs/ n^+ -Si bonding interface obtained by SAB and the front metal grid design, which is adapted for these low concentrations.

3J cells with an efficiency of $25.2 \pm 1.8\%$ at 15 suns and 2J cells with efficiencies of $21.1 \pm 1.5\%$ at 1 sun and $23.7 \pm 1.7\%$ at 10 suns have been demonstrated. The 2J cell results are remarkable, representing the best reported to date 2J 2T III-V on Si tandem cell efficiency at 1 sun and the best 2J 2T Si-based tandem cell efficiency under low concentration. Even higher efficiencies could be obtained by the implementation of the design improvements already mentioned in chapter 3.

Chapter 5

Conclusions

In this PhD work, wafer-bonded III-V on Si tandem solar cells were studied, including the design optimization, the fabrication process and the characterization. In the next section, the main results obtained will be presented, followed by the perspectives.

5.1 Main results

Alternative bonding approaches to the well known SAB technique have been evaluated for the fabrication of III-V on Si solar cells: hydrophilic GaAs//Si bonding with native oxides, hydrophilic GaAs//Si bonding with UV-O₃ oxidizing treatment and hydrophilic GaAs//GaAs bonding by growing a GaAs epitaxial layer on Si. Near defect free bonding interfaces, characterized by SAM, are obtained for hydrophilic wafer bonding using UV-O₃ and by epi-GaAs//GaAs wafer bonding approaches. However, the oxides formed at the bonding interface degrade the electrical conductivity resulting in diode-like I - V curves. Despite this non-ideal behavior, 3J solar cells fabricated with epi-GaAs//GaAs novel approach present FF values as high as 80%. Unlike SAB, epi-GaAs//GaAs bonding has the advantages of not requiring ultra-high vacuum or ion beam surface bombardment, opening a new path for III-V on Si integration with a more promising industrialization potential.

For a further characterization and comprehension of the bonding interface, original test devices conceived at CEA have been fabricated, allowing to evaluate the interface resistance. Even if the surface doping of these structures is not the same as for the tandem solar cells, R_{int} evaluated this way can be interpreted as an upper limit, allowing to conclude that the interface resistance does not limit the performance of the tandem cells fabricated by SAB. I - V measurements as a function of temperature have revealed the presence of a potential barrier for SAB bonding due to Ar beam induced defects. At room temperature,

thermal energy is enough to overcome this barrier producing an ohmic behavior. However, the conductivity decreases at lower temperatures showing diode-like I – V curves. This dependence on temperature suggests that the conduction mechanism through the interface can be described by the thermionic emission model.

Experimental characterizations and simulations were performed in order to optimize the III-V and Si subcell design and fabrication process, leading to record efficiencies. For the AlGaAs top subcell of the 2J, this includes the use of an AlInP window together with a GaInP emitter, forming an n-GaInP/p-AlGaAs heterojunction, which allowed to keep the 1.7 eV optimum top cell bandgap and led to a I_L top subcell improvement of 7.3%, thanks to the short wavelength enhanced performance. In addition, the increase in light transmission to the bottom subcell by reduction of the GaAs bonding layer thickness and the use of a higher bandgap AlGaAs tunnel junction resulted in a bottom subcell I_L improvement of 6.8% compared to the first designs.

For the Si bottom subcell, simulations allowed to identify the key factors that limit the performance, being the bulk lifetime the most critical characteristic in the thick Si cells used. In the case of III-V//Si interfaces with high SRV, a highly doped emitter is crucial to passivate the surface, minimizing recombination and thus increasing V_{OC} , outweighing the drop in I_{SC} due to lifetime degradation. Back surface passivation is also important, especially to increase collection of infrared wavelengths that are only absorbed in the Si bottom subcell.

Different diffusion and implantation processes for the emitter formation were studied. Implantation processes showed less bulk lifetime degradation and smoother surfaces, thereby allowing bonding without chemical-mechanical planarization. Higher doping levels can be obtained this way, resulting in a better surface passivation. However, the presence of iron metallic impurities, which are probably activated during high temperature annealing, still limit the performance of the Si subcells.

The ARC was optimized by transfer-matrix simulation methods. Using a $\text{Si}_3\text{N}_4/\text{SiO}_2$ double-layer, instead of the initial Si_3N_4 single-layer, the reflectance in the bottom subcell absorption region was reduced from around 10-20% to only 5%, which allowed current mismatch reduction for the 3J cell.

This design and fabrication process optimization allowed to obtain record tandem cell efficiencies, which were measured using the new Hybrid Corrected Pseudo-Isotype (HCPI) I – V characterization method, specially adapted for MJSC under concentrated light. The so-called HCPI method is fast, low cost and easily adaptable for the development of new MJSC technologies because it does not require perfectly matched component cells. Instead, Si single-junction cells with optical filters are used as pseudo-isotypes and the measured

subcell concentrations, X_i , are corrected with the spectral mismatch correction factors, M_i , which are calculated from the simulator spectrum and EQE measurements. The use of a high-speed CMOS spectroradiometer enables the measurement of the multi-flash simulator spectrum and hence the calculation of M_i to correct the spectral mismatch. The spectrum adjustment is carried out using the pulse spectral variation during the lamp cool down and hence no additional tunable elements are needed, except AM1.5 or AM0 filters to reduce the Xe emission lines.

This method has been applied for the characterization of 2J and 3J 2T III-V on Si tandem solar cells, obtaining the $I-V$ characteristics under low concentrations. M_{bottom} differed from unity by up to 3.2% for the 2J cell and by 2.2% for the 3J cell, showing the importance of properly applying this spectral correction which directly affects the concentration and hence the measured efficiency. The relatively low series resistance, $R_S = 0.35 \Omega\text{cm}^2$ for the 2J and $R_S = 0.38 \Omega\text{cm}^2$ for the 3J, enabled high FF values, over 80% for the 2J and up to 90% for the 3J, thanks to the highly conductive n^+ -GaAs// n^+ -Si bonding interface obtained by SAB and the front metal grid design, which is adapted for these low concentrations.

3J cells with an efficiency of $25.2 \pm 1.8\%$ at 15 suns and 2J cells with efficiencies of $21.1 \pm 1.5\%$ at 1 sun and $23.7 \pm 1.7\%$ at 10 suns have been demonstrated. The 2J cell results are remarkable, representing the best reported to date 2J 2T III-V on Si tandem cell efficiency at 1 sun and the best 2J 2T Si-based tandem cell efficiency under low concentration.

Despite these 2J record efficiencies, these cells are still less efficient than the best Si single-junction solar cells reported in the literature [33]. This is because the full potential of this 2J technology (45% at 1 sun from detailed balance calculations) is still far away from being reached.

In the perspectives, some strategies to improve cell performance are presented, together with wafer bonding challenges that still need to be addressed and additional characterizations that could be performed.

5.2 Perspectives

Even though promising results have been obtained with the novel epi-GaAs//GaAs hydrophilic bonding approach, no other surface treatments are known that could produce thinner and more conductive interfacial oxides. The better results obtained by the SAB technique favor its use, despite being much more complex. With this respect, it is interesting to note that some companies like EVG are developing new SAB tools for high-throughput manufacturing environments, which could make SAB economically viable.

As discussed in chapter 3, not all the optimizations studied were applied to the 2J and 3J tandem cells measured by I – V . Therefore, even higher efficiencies could be obtained by the implementation of BLII doping profiles and $\text{SiO}_2/\text{Si}_3\text{N}_4$ back surface passivation to the Si bottom subcell. In addition, as demonstrated by the simulations and some recent 3J realizations reported in the literature [79], much higher efficiencies are possible by the use of thinner Si cells together with photon recycling techniques, like back surface texturing or diffraction gratings. A good back Si surface passivation is essential in this case, being the use of poly-Si thin layers the most promising technique. The poly-Si passivation can also be applied to the front surface, minimizing recombinations in the damaged III-V//Si interface and therefore enabling less doped Si emitter profiles. CEA is also working in this kind of passivation [198] and III-V on Si solar cells using this technique are currently being manufactured.

In order to further optimize the subcells and to increase the comprehension of the fabrication process impact on performance, it would be useful to complete the *IQE* experimental analysis with spectral electroluminescence, $\text{EL}(\lambda)$, characterization. This technique would enable to measure the individual subcell V_{OC} , the derivation of the individual subcell I – V curves [224–226] and the calculation of the external radiative emission efficiency (ERE), which is the best figure of merit to compare the quality of solar cells of different materials [227].

In addition, different collaborations were established with other research organizations. The Research Center for Advanced Science and Technology (RCAST), of the University of Tokyo, is performing laser beam induced current (LBIC) mapping characterization of our tandem cells in order to study the local luminescent coupling (LC) effect between the subcells [293].

The GeePs laboratory, standing for *Génie Electrique et Electronique de Paris*, is also studying our III-V on Si solar cells by capacitance–voltage (C – V) characterization. This technique adapted to MJSC allows to determine the doping concentration and the built-in voltage of each of the junctions [294].

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Appendix A

Quantum efficiency and reflectance characterization

External Quantum Efficiency (EQE) and Reflectivity (R) allow to assess the photon absorption, reflection and photo-generated carrier collection efficiency for every different light wavelength. This data is extremely useful to quantify the loss mechanisms due to recombination and reflection, enabling the optimization of the different subcell layers and ARC.

The EQE is the ratio between the number of photons of a given wavelength incident on the solar cell and the number of carriers collected. If all photons of a certain wavelength are absorbed and all the resulting photo-generated carriers are collected, then the quantum efficiency at that particular wavelength is unity [295].

The EQE of a solar cell includes the effect of optical losses such as transmission and reflection. However, taking into account only the light that is actually absorbed, gives a better insight of the recombination losses. Internal Quantum Efficiency (IQE) refers to the efficiency with which photons that are absorbed, and not reflected or transmitted out of the cell, generate carriers that are collected. By measuring the R and Transmission T of a device, the EQE can be corrected to obtain the IQE following equation A.1. In the case of this study, the bottom subcells are made of a 525 μm -thick Si substrate and have a full wafer back metal contact which reflects back most of the light. Therefore, to a good approximation T can be considered zero.

$$IQE(\lambda) = \frac{EQE(\lambda)}{1 - R(\lambda) - T(\lambda)} \quad (\text{A.1})$$

EQE and R measurements are performed using a conventional system as reported in references [296, 297]. The EQE setup includes a lock-in amplifier, a low-noise pre-amplifier,

a monochromator and a calibrated detector. A Xe arc lamp positioned at the entrance of the monochromator produces a white light source that is filtered and chopped at the lock-in frequency. In addition, light produced by halogen lamps with band-pass filters is guided by optical fibers and used as light bias, forcing the measured junction to generate the smallest photocurrent and hence becoming the current-limiting junction. Finally, a 4-quadrant source-meter is used to bias the cell so that the subcell being measured is at 0 V and thus at J_{SC} .

The actual measured quantity is the Spectral Response, $SR(\lambda)$, and from this the EQE can be calculated with the following equation:

$$EQE(\lambda) = \frac{h c}{q \lambda} \cdot SR(\lambda) \quad (A.2)$$

where h is the Planck constant, c is the speed of light, q is the electron charge and λ is the light wavelength.

The subcell photo-generated currents under the reference spectrum G_{λ}^* can be estimated using equation A.3.

$$I_L = \int_{\lambda} SR(\lambda) \cdot G_{\lambda}^* d\lambda \quad (A.3)$$

The current-matching ratio, CM , determined using equation A.4, can be used to compare the photo-generated currents of two subcells. Taking top and bottom as an example, if $CM^{(top/bottom)} > 1$, the bottom subcell limits the current and on the contrary, if $CM^{(top/bottom)} < 1$, the top subcell is the one limiting the current. $CM^{(top/bottom)} = 1$ indicates perfect current-matching between the subcells.

$$CM^{(top/bottom)} = \frac{I_{L \text{ top}}}{I_{L \text{ bottom}}} \quad (A.4)$$

Appendix B

List of publications

Peer-reviewed journal articles

1. **E. Veinberg-Vidal**, L. Vauche, K. Medjoubi, C. Weick, C. Besançon, P. Garcia-Linares, A. Datas, A. Kaminski-Cachopo, P. Voarino, P. Mur, J. Decobert and C. Dupré. “Characterization of Dual-Junction III-V on Si Tandem Solar Cells with 23.7% Efficiency Under Low Concentration.” *Progress in Photovoltaics: Research and Applications*, (accepted for publication).
2. L. Vauche, **E. Veinberg-Vidal**, T. Desrues, A. Lanterne, M. Coig, F. Milesi, C. Lecouvey, C. Morales, K. Medjoubi, C. Jany, S. Dubois, F. Fournel and P. Mur. “Optimization of Silicon Bottom Subcell Adapted for Wafer-Bonded Two-Terminal III-V on Si Multi-Junction Solar Cells.” *Solar Energy Materials & Solar Cells*, (submitted).
3. B. M. Y. Jeco, **E. Veinberg-Vidal**, L. Vauche, K. Yoshida, R. Tamaki, N. Ahsan, and Y. Okada. “Luminescent Coupling Effect in Wafer-Bonded III-V on Silicon Multijunction Solar Cells.” *Journal of Photonics for Energy (JPE)*, (submitted).
4. B. M. Y. Jeco, **E. Veinberg-Vidal**, L. Vauche, N. Ahsan, and Y. Okada. “Temperature Dependence of Wafer-Bonded III-V on Silicon Multijunction Solar Cells with Luminescent Coupling Effect.” *Journal of Photonics for Energy (JPE)*, (submitted).

Conference papers

1. C. Leon, A. Brezard-Oudot, S. Le Gall, M. E. Gueunier-Farret, J. P. Kleider, L. Vauche, K. Medjoubi, and **E. Veinberg-Vidal**. “Application de la technique de caractérisation Capacité-Tension à l’étude des cellules tandem.” *Journées nationales du photovoltaïque (JNPV)*. Dourdan, 2018.

2. L. Vauche, **E. Veinberg-Vidal**, T. Desrues, A. Lanterne, M. Coig, F. Milesi, C. Lecouvey, C. Morales, C. Jany, K. Medjoubi, P. Mur. "Silicon Bottom Subcell Optimization for Wafer-Bonded III-V on Si Multijunction Solar Cells." In Proceedings of the 7th World Conference on Photovoltaic Energy Conversion (WCPEC-7), 3. Waikoloa, Hawaii, 2018.
3. R. Cariou, K. Medjoubi, L. Vauche, **E. Veinberg-Vidal**, S. Park, M. Baudrit, P. Voarino, P. Mur and B. Boizot. "Evaluation of III-V/Si Multi-Junction Solar Cells Potential for Space." In Proceedings of the 7th World Conference on Photovoltaic Energy Conversion (WCPEC-7). Waikoloa, Hawaii, 2018.
4. **E. Veinberg-Vidal**, L. Vauche, K. Medjoubi, C. Weick, P. Garcia-Linares, A. Datas, A. Kaminski-Cachopo, C. Jany, P. Voarino, M. Baudrit, P. Mur and C. Dupré. "Characterization of III-V on Si Tandem Solar Cells under Low Concentration Using a Pulsed Solar Simulator and Component Cells." In Proceedings of the 27th Photovoltaic Science and Engineering Conference (PVSEC-27). Shiga, Japan, 2017.
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