

UNIVERSIDAD POLITÉCNICA DE MADRID
Escuela Técnica Superior de Ingenieros de Telecomunicación



Assessment of Ge-based virtual substrates for III-V photovoltaics

DOCTORAL THESIS

Submitted for the degree of Doctor by:

Víctor Manuel Orejuela Sánchez

Grado en Física y Máster en Materiales Avanzados, Nanotecnología y
Fotónica

Madrid, 2024



UNIVERSIDAD POLITÉCNICA DE MADRID
Escuela Técnica Superior de Ingenieros de
Telecomunicación

Doctoral Degree in Photovoltaic Solar Energy

Assessment of Ge-based virtual substrates for III-V photovoltaics

DOCTORAL THESIS

Submitted for the degree of Doctor by:

Víctor Manuel Orejuela Sánchez

Grado en Física y Máster en Materiales Avanzados, Nanotecnología y
Fotónica

Under the supervision of:

Dr. Iván García Vara

Madrid, 2024

Title: Assessment of Ge-Based Virtual Substrates for III-V Photovoltaics

Author: Víctor Manuel Orejuela Sánchez

Doctoral Programme: Doctoral Degree in Photovoltaic Solar Energy

Thesis Supervision:

Dr. Iván García Vara, Associate Professor, Universidad Politécnica de Madrid (Supervisor)

External Reviewers:

Thesis Defense Committee:

Thesis Defense Date:

Al empeño y bienestar mental

“¿Qué es esto? ¿Romanes eunt domus? ¿Gente llamada romanos ir la casa?”

- Centurión en ‘La vida de Brian’

“Certeza de muerte... mínima esperanza de éxito... ¿a qué esperamos?”

- Gimli en ‘El retorno del rey’

Table of Contents

<i>Agradecimientos</i>	<i>viii</i>
<i>Abstract</i>	<i>xi</i>
<i>Resumen</i>	<i>xiii</i>
<i>List of Figures</i>	<i>xv</i>
<i>List of Tables</i>	<i>xxvii</i>
<i>List of Abbreviations and Acronyms</i>	<i>xxix</i>
<i>List of Symbols</i>	<i>xxx</i>
<i>List of Constants</i>	<i>xxxv</i>
1. Introduction	1
1.1. Motivation	2
1.1.1. Global warming	2
1.1.2. Solar energy as solution	4
1.2. Semiconductors in electronics and solar energy.....	6
1.2.1. Silicon technology.....	6
1.2.2. Ge and III-V high efficiency technology	7
1.2.3. Integration of Si and III-V/Ge.....	10
1.2.3.1. GaP/Si technology.....	11
1.2.3.2. Ge deposition on Si	13
1.2.3.3. Effects of threading dislocations on device performance	18
1.2.4. Multijunction solar cells on Ge-based substrates at IES-UPM	22
1.2.4.1. Ge Si virtual substrates with thick Ge layer functioning as bottom cell	23
1.2.4.2. Ultra-thin Ge Si	27
1.2.4.3. Germanium-On-Nothing.....	29
1.3. Objective and Thesis organization.....	31
2. Methodology	34
2.1. Epitaxial deposition by MOVPE	35
2.1.1. MOVPE fundamentals	35
2.1.2. In-situ Reflectance Anisotropy Spectroscopy.....	37
2.1.2.1. In-situ reflectivity.....	39
2.2. Epitaxial material characterization techniques	41
2.2.1. Electrochemical capacitance-voltage	41
2.2.2. Atomic force microscopy	44
2.2.3. Transmission electron microscopy.....	45
2.2.3.1. High-resolution transmission electron microscopy	48
2.2.3.2. Bright-field transmission electron microscopy.....	49

2.2.3.2.1 Annular bright-field imaging	50
2.2.3.3. Annular dark-field imaging.....	51
2.2.4. Secondary ion mass spectrometry	51
2.2.5. Scanning electron microscopy.....	53
2.2.5.1. Electron channelling contrast imaging	54
2.2.5.2. Electron backscatter diffraction	55
2.3. Photovoltaic devices characterization.....	57
2.3.1. Quantum efficiency and reflectance	57
2.3.2. Current-Voltage curves	59

Block I: Ge-Based substrates analysis

3. Characterization of Ge Si virtual substrates.....	62
3.1. In-situ measurements during the MOVPE growth process.....	64
3.1.1. Pre-deposition analysis.....	65
3.1.2. Ongoing III-V deposition assessment	66
3.2. Lattice deformation	69
3.3. Interface analysis.....	73
3.3.1. Effect of MOVPE thermal load on Ge surface	76
3.4. Threading dislocations impact on III-V layers.....	77
3.4.1. Study of Ga(In)As surface morphology.....	81
3.5. Discussion and conclusions	85
4. Performance characterization of triple junction solar cells on GON substrates	89
4.1. In-situ measurements during epitaxial deposition.....	91
4.2. Electrical characterization	92
4.3. Solar device detachment.....	93
4.4. Discussion and conclusions	94

Block II: Study of diffusion in Ge

5. Solid state diffusion in Ge	98
5.1. Introduction.....	99
5.1.1. Modeling of the diffusion phenomenon	100
5.1.1.1. Identification of profiles for different concentration-dependent diffusion coefficient	101
5.2. Diffusion of group III and V atoms in Ge	103

5.2.1. Group III in Ge	103
5.2.2. Group V in Ge	103
5.3. Ge solid-phase cross-diffusion into III-V epilayers	107
5.4. Study of the As diffusion in Ge	108
5.4.1. Impact of AsH ₃ preexposure.....	110
5.4.1.1. Morphological characterization	111
5.4.1.2. Doping profile measurements	112
5.4.1.2.1 SIMS profile measurements	115
5.4.2. Effect of GaAs deposition following AsH ₃ preexposure	117
5.4.2.1. Doping profile measurements	117
5.4.2.1.1 SIMS profile simulations.....	119
5.4.3. Cooldown influence on GaAs/Ge MOVPE growths	121
5.5. Discussion and conclusions	122
6. Summary, conclusions and future works.....	125
6.1. Summary sand conclusions of the main research findings	127
6.2. Future works.....	130
Appendix A	132
A.1. Integrating the Crank-Nicolson method with Newton-Raphson root-finding	133
A.2. The fourth-order Runge-Kutta method	138
A.3. Comparison between numerical methods	141
Bibliography	145
Publications and conferences.....	166

Agradecimientos

Quisiera, en primer lugar, agradecer a la entidad que me permitió alcanzar el objetivo de obtener el título de doctor. Gracias al Ministerio de Ciencia e Innovación por financiar este proyecto de tesis a través de la beca de Formación del Personal Investigador (FPI), número de identificación PRE2019-088437. También agradezco al ya extinto proyecto VIGNEMALE, que hizo posible esta subvención. Un agradecimiento especial a Iván García e Ignacio Rey-Stolle por considerarme para esta ayuda y permitirme participar en el grupo de semiconductores III-V. En particular, a Iván García por su mentoría y ayuda para pulir este escrito con su vasta experiencia.

Agradezco también la acogida en la Universidad Politécnica de Madrid (UPM), especialmente al Instituto de Energía Solar (IES), perteneciente a la Escuela Superior de Ingenieros de Telecomunicaciones (ETSIT) en el campus de Moncloa, donde realicé mis experimentos y análisis. Aquí adquirí conocimientos en una profesión que considero noble y sacrificada, y viví momentos inolvidables rodeado de máquinas de caracterización y productos químicos (en un ambiente seguro, por supuesto), tanto en el laboratorio como en la sala del reactor MOVPE. No puedo olvidar a Elisa García-Tabarés de la Universidad Carlos III (campus de Leganés), cuya colaboración fue crucial para mi trabajo gracias a las mediciones que nos proporcionó.

En el ámbito personal, mi mayor agradecimiento es para mi familia, que me apoyó económicamente en mi carrera académica. En especial, a mi madre, Milagros, quien sacrificó mucho para que yo pudiera ser graduado y, finalmente, el primer doctor en la familia. Parte de este título es, sin duda, de ella. Agradezco también a mis fantásticos compañeros de trabajo, desde mis iguales doctorandos hasta los habilidosos técnicos. La cercanía y el cariño que compartimos hicieron más llevadero el camino hacia el doctorado.

Mi corta estancia en la Escuela Técnica Superior de Ingeniería de Sistemas Informáticos en el campus sur me permitió conocer a Kiane Alves, Cristina Sanz y Juan Santamaría, a quienes aprecio. Agradecimientos y cálidos abrazos para mis compañeros habituales en el campus de Moncloa: Carlos Bueno, Álvaro Manuel Medrano, Inés Durán, Luis Javier San José, Mario Martínez, Alicia López de Ceballos, Jorge Rodríguez, Daniel Gómez, Almudena García, Ignacio Izquierdo, Ricardo Moruno, Juan Manuel Redondo y mi Alfonso González del Valle, por los buenos momentos compartidos. Recuerdo con nostalgia las primeras semanas en el IES compartiendo despacho en el Patio casi vacío por la COVID, donde conocí a Javier Alfonso Macías, Marina Delgado y al chef y organizador por excelencia, Pablo Martín. No puedo olvidar a Luis Cifuentes, que nos alegra (y agota) con su interminable lista de chistes malos y juegos de palabras; a Aitana Cano, por su apoyo emocional en mis puntuales momentos difíciles; a la

Dra. Clara Sánchez-Pérez, por su ayuda y consejos cercanos; y a Pablo Fernández, por su inestimable ayuda en algunos aspectos de mi investigación. Gracias a todos, y no olvidaré los grandes momentos que pasamos tanto en el IES como fuera, con unas bebidas o en nuestros viajes a casas rurales. Por último, y no menos importante, una mención a Jesús Bautista por su ayuda técnica y su toque de humor poco sutil. Si alguien lee esto, debe saber que todos mis compañeros aquí mencionados son grandes investigadores y técnicos cuya profesionalidad merece los mejores éxitos. Dudar de ello sería un completo desatino.

También agradezco, con ligero dolor de cabeza, al arsénico y al germanio por dejarse caracterizar. Gracias, queridos elementos, aquí está todo lo que me habéis revelado.

Finalmente, me gustaría compartir un mensaje personal. La realización de este doctorado ha coincidido con una etapa de superación y descubrimiento personal. Con la obtención del título de doctor, cierro un capítulo que recordaré con cariño y doy paso al siguiente, donde seguiré mejorando como persona, descubriéndome y (espero) dedicándome a la investigación. Estoy orgulloso de haber logrado este objetivo, lo que me hace valorar más a quienes están en una en similar situación “doctoril”.



Abstract

Silicon has been the dominant material in electronics due to its abundance and cost-effectiveness, leading to a well-established industry and widespread use. This also makes it a major component in photovoltaics, with about 95% of solar modules made from silicon. However, silicon-based photovoltaic technology is nearing its maximum efficiency, and further improvements are increasingly difficult and expensive. Consequently, researchers are exploring alternative materials. III-V semiconductors, although more costly, promise higher efficiencies. Their integration into tandem solar cells on silicon substrates is well-researched, but a 4.2% lattice mismatch between silicon and common III-V materials, such as gallium arsenide, poses a significant challenge. This mismatch causes defects that reduce the efficiency of solar devices.

To address this, one approach uses germanium, which has a similar lattice constant and thermal expansion coefficient to III-V materials. This Thesis investigates germanium-based technologies to overcome lattice mismatch challenges in silicon photovoltaic systems. It examines alternative solutions and their impact on the performance of solar devices, focusing on materials grown by MOVPE deposition.

The study initially explores two alternative substrates for III-V epitaxial deposition in tandem solar cells. The first substrate uses silicon's cost-effectiveness and availability, featuring a novel structure with an ultra-thin layer of germanium (a few nanometers thick) epitaxially grown on silicon. The research characterizes these Ge|Si virtual substrates to predict potential issues from lattice mismatch. It specifically looks at how pre-existing defects propagate into subsequent layers, such as gallium arsenide deposited by MOVPE, affecting layer quality. Initial findings show significant plastic deformation and high densities of threading dislocations in both the ultra-thin Ge layer and the gallium arsenide layer.

The second alternative involves germanium-on-nothing substrates, developed by UMICORE and IMEC, which create a predefined structure in the germanium wafer without silicon. This structure enables the detachment of a tunable thickness germanium foil (approximately 7 μm in this study) after epitaxy or processing, leaving the remaining germanium substrate intact. Triple-junction solar cells (GaInP/GaInAs/Ge) were grown on these substrates and electrically characterized. These cells show high reproducibility comparable to those on standard germanium substrates, though with minor efficiency losses due to increased back surface recombination in the thin Ge subcell.

The final segment investigates arsenic diffusion during gallium arsenide deposition on germanium substrates using MOVPE. Understanding this diffusion is crucial for optimizing Ge-based virtual substrates. The study examines how pre-treatment conditions affect arsenic diffusion, noting that arsine exposure creates germanium vacancies, enhancing arsenic diffusion. Simulations confirm that arsenic diffusivity depends on concentration, with findings challenging previous beliefs by showing a linear, rather than quadratic, relationship with electron concentration, as opposed to established ion implantation studies.

Resumen

El silicio ha sido el material dominante en electrónica debido a su abundancia y bajo coste. Esto también lo hace el material por excelencia en energía fotovoltaica, con el 95% de los módulos solares fabricados con este material. Sin embargo, la tecnología basada en silicio está alcanzando su máxima eficiencia, y mejorarla se vuelve cada vez más costoso. Por eso, se exploran diseños y materiales alternativos como los semiconductores III-V, que aunque más caros, pueden aumentar la eficiencia. La integración de estos semiconductores, como el arseniuro de galio, en células solares en tándem sobre silicio enfrenta el reto del desajuste de red, aproximadamente del 4,2%, que induce defectos que afectan negativamente la conversión de fotones en electricidad.

Para solventar este problema, se estudia el uso del germanio, que tiene una constante de red y coeficiente de expansión térmica similares a los de los materiales III-V. Esta tesis explora tecnologías basadas en germanio para abordar el desajuste de red en sistemas fotovoltaicos basados en silicio, investigando soluciones alternativas y sus impactos en el rendimiento de los dispositivos solares, todos ellos crecidos por epitaxia MOVPE.

El estudio se enfoca en dos sustratos alternativos para la epitaxia de III-V en células solares en tándem. El primero utiliza silicio con una capa ultrafina de germanio crecida sobre él. Esta investigación se centra en caracterizar estos sustratos virtuales de Ge|Si para entender los problemas del desajuste de red y examinar la propagación de defectos en capas posteriores de arseniuro de galio. Las medidas iniciales muestran deformación plástica y una alta densidad de dislocaciones tanto en la capa de Ge como en la de arseniuro de galio depositada epitaxialmente.

La segunda alternativa son los sustratos de germanio sobre micropilares, desarrollados por UMICORE e IMEC, que permiten crear una estructura en la oblea de germanio sin depender del silicio. En este estudio, se crecieron células solares de triple unión GaInP/GaInAs/Ge sobre estos sustratos reutilizables, mostrando alta reproducibilidad y pequeñas pérdidas de eficiencia debido a la recombinación en la subcélula delgada de Ge.

Finalmente, se investiga la difusión de arsénico durante el proceso de epitaxia de arseniuro de galio en sustratos de germanio. Comprender esta difusión es crucial para optimizar los sustratos virtuales basados en Ge. El estudio analiza cómo el pretratamiento en el proceso MOVPE afecta la difusión del arsénico, observando que la exposición a arsina genera vacantes de germanio que facilitan la difusión de arsénico. Las simulaciones numéricas muestran que la difusividad del arsénico depende de la concentración y revela una dependencia lineal con la

concentración de electrones, refutando el conocimiento previo que sugería una dependencia cuadrática, basada comúnmente en estudios de difusión mediante implantación iónica.

List of Figures

Figure 1.1. Temporal trends in global mean temperature from 1850 onward. The red line represents the mean temperature, while the surrounding grey lines delineate the upper and lower bounds of the 95% confidence intervals. Source: <https://ourworldindata.org/co2-and-greenhouse-gas-emissions>..... 2

Figure 1.2. Comparative images depicting Lake Powell (Arizona and Utah) in 1999 (left) and 2014 (right), illustrating the impact of prolonged drought conditions. Source: <https://climate.nasa.gov/images-of-change>..... 3

Figure 1.3. Graph of the irradiance for solar spectra AM0 (red) and AM1.5G (blue). Spectra are divided into three ranges: UV, visible and IR. Tag positioned adjacent to blue valleys denote the absorption bands for specific molecules in the atmosphere..... 5

Figure 1.4. Band diagram of a semiconductor. When the energy photon is below the bandgap, electrons remain in the valence band (below) without promotion to the conduction bandgap (top). Conversely, photon energies exceeding the bandgap permit electron promotion, creating a hole in the valence band where the electron was originally located..... 6

Figure 1.5. Graph of the irradiance for solar spectra AM1.5G (black line). Spectra are divided into three ranges: UV, visible and IR. The green-shaded spectrum area indicates the product of SR and the spectral irradiance in a typical Ge solar cell 8

Figure 1.6. Graph depicting the relationship between bandgap and lattice constant of III-V materials. The shaded area highlights semiconductors with similar lattice parameters, prevalent in typical electronics applications like PV 9

Figure 1.7. Graph of the spectral irradiance for solar spectra AM1.5G (black line). Spectra are divided into three ranges: UV, visible and IR. Shaded areas represent the product of SR and the spectral irradiance for each layer, in this case, the GaInP/GaInAs/Ge TJSC 10

Figure 1.8. Schematic depiction of GaP-based layers on Si. Design (a) showcases a GaP nucleation layer on Si, serving as a platform for the deposition of other III-V materials, accompanied by a dislocation filter layer. The conceptual illustration on the left highlights the presence of misfit and potential threading dislocations within the dislocation filter. In design (b), the configuration remains consistent, albeit with a graded $\text{GaAs}_x\text{P}_{1-x}$ buffer layer. Layer thicknesses in the representations are not drawn to scale 12

Figure 1.9. TDD values for three different methods of Ge deposition on Si as a function of Ge thickness. The filled circles represent data from [64], the orange squares denote values obtained from [67] and the green diamonds are extracted from [66]. The colored tags indicate the separation space among patterned strips (orange) and the TDD values when arsenic doping is not conducted for the same process (green)..... 16

Figure 1.10. Plots illustrating J_0/J_0^{max} as a function of TDD values for GaAs (a) and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ (b), doped as both n-type and p-type semiconductors with a concentration of 10^{17} cm^{-3} for all cases. Dashed lines indicate the value of TDD where the ratio experiences a considerable and constant increase 20

Figure 1.11. Schematic depiction of two Ge|Si virtual substrate designs. Design I illustrates a TJSC configuration with a sufficiently thick Ge layer (a few microns) serving as the active bottom cell. In Design II, the TJSC configuration is maintained, but the Ge layer is intentionally thin (a few nanometers), functioning solely as a bridge between GaInAs and Si 23

Figure 1.12. Frontal perspective of the TJSC with visible cracks traversing the device's surface. Highlighted by yellow arrows are instances of these cracks for reference 24

Figure 1.13. Structure of a metamorphic $\text{GaInP}/\text{Ga}_{0.933}\text{In}_{0.067}\text{As}/\text{Ge}/\text{Si}$, featuring a CGB to facilitate the accommodation of lattice constants between Ge and $\text{Ga}_{0.933}\text{In}_{0.067}\text{As}$ 25

Figure 1.14. (a) EQE of the top and middle cells in the TJSC under examination. The dots represent experimental results for the TJSC on standard Ge substrates (yellow orange) and the TJSC with a thinned $\text{Ga}_{0.933}\text{In}_{0.067}\text{As}$ middle cell on a Ge|Si virtual substrate (green). (b) Representative J-V measurements of the TJSC developed on Ge|Si with varied thinning and In content, in comparison to the conventional design on a standard Ge substrate. Inset: Nomarski microscope image of the TJSC with thinned GaInAs on Ge|Si after growth..... 26

Figure 1.15. Simulated values for J_{sc} , V_{oc} , and efficiency at 1-sun for the optimized triple-junction solar cell on Ge|Si versus the thickness of the Ge layer, considering three different design scenarios 27

Figure 1.16. (a) Experimental EQEs of GaInAs/Ge|Si. (b) Light J-V curves of the same DJSC configuration. Inset: Schematic representation of the GaInAs/Ge|Si DBJS 28

Figure 1.17. Schematic representation of the iterative fabrication process for Ge-on-Ge engineering: (a) A Ge wafer undergoes (b) lithography and dry etching steps to create micropitches, initiating the formation of a Ge-on-Ge structure. Subsequent annealing facilitates the coalescence of micropitches until (c) complete merging occurs, resulting in a suspended foil. (d) III-V semiconductors are epitaxially deposited onto the foil to establish the future solar device after undergoing prior processing. Finally, (e) the heterojunction is detached, and the remaining Ge is reused after (f) reconditioning, returning to step (a). This iterative process continues until the Ge wafer is depleted 30

Figure 1.18. The Lift-off of a Ge foil from a Ge-on-Ge engineered substrate, with the foil measuring $1.3\ \mu\text{m}$ in thickness..... 30

Figure 1.19. EQE measurements obtained from devices fabricated on bulk Ge substrate (blue) are compared with those from devices fabricated on Ge-on-Ge engineered substrate (red) 31

Figure 2.1. Sequential steps of a MOVPE process at IES-UPM. The substrate enters the reactor from the glove box, where it is warmed by the IR-Heater while precursors are introduced. These precursors undergo cracking, depositing desired atoms (blue and red circles) onto the substrate while byproducts (yellow and brown circles) are evacuated. This cycle continues until the desired layer/s are fully deposited, ready to be extracted from the MOVPE system. 36

Figure 2.2. RAS spectrum for various GaAs (001) surface reconstruction. This figure was sourced from [106]..... 38

Figure 2.3. Reflectance graphs for AlAs-based deposition on GaAs. (a) Illustration of the change in the period with varying GR. (b) Illustration of the change in signal intensity and period as the Ga content increases in the ternary AlGaAs alloy. The labels d_{max} and d_{min} indicate the points of maximum and minimum interference, respectively. (Source: Information notes of www.laytec.com) 40

Figure 2.4. (a) Schematic illustration of the ECV measurement method with labeled components. (b) Representation of the etching process in ECV, depicting the procedure in p-type (upper half) and n-type (lower half) semiconductors. Blue circles denote electrons, white circles represent holes, red circles depict component atoms in the sample, and green circles denote atoms from the electrolyte..... 41

Figure 2.5. Carrier profile (p-type) resulting from boron diffusion into Si. As referenced in [112], this profile denotes the emitter region of the solar cell under investigation 43

Figure 2.6. AFM measurement representation. The AFM tip scans the sample surface, inducing a slight deflection in the cantilever. This deflection alters the laser reflection, translated into an intensity map by the detector. (Source: <https://physik.uni-greifswald.de/en/research-groups/soft-matter-and-biophysics-prof-christiane-helm/methods/afm-atomic-force-microscope>)..... 45

Figure 2.7. AFM images of defects formed on GaInP deposited on a Ge substrate: (a) arrowhead defect and (b) asymmetric inverted pyramid defect. These images are sourced from [19]..... 45

Figure 2.8. Schematic representation of a transmission electron microscope, illustrating its components. (Source: <https://www.britannica.com/technology/transmission-electron-microscope>)..... 46

Figure 2.9. Cross-sectional TEM images illustrating the reduction of TDD with increasing annealing temperature (indicated in the upper left corner of each image). Yellow asterisks denote a thin film of GaInAs/GaAs within the GaAs dislocation filter. Images are sourced from [121]..... 47

Figure 2.10. SEM images of InSb nanowires after deposition of InAs (a) and InP (b) materials. HRTEM micrographs highlight the interfaces between these materials ((c) for InAs and (d) for InP). Yellow arrows indicate the disruption of atomic arrangements at the interfaces. Images are sourced from [123] 48

Figure 2.11. BF-TEM image showing epitaxially deposited GaN on a GaN/sapphire substrate. Examples of dislocations are highlighted by arrows labeled as A and B. Image is sourced from [124]..... 49

Figure 2.12. (a) ABF-STEM image and (b) ADF-STEM image of GaN deposited on sapphire. (c) Intensity profiles obtained from the lines indicated in the images above. The upper tags denote the camera length in millimeters. Images are sourced from [125]..... 50

Figure 2.13. Schematic depiction of secondary ion mass spectrometry. Image source: [126] 52

Figure 2.14. SIMS profiles of P and Sb vs. depth in $\text{GaP}_x\text{Sb}_{1-x}/\text{GaSb}$ structure obtained by processing GaSb in phosphorous vapors. The figure is sourced from [129]. 52

Figure 2.15. Schematic diagram illustrating the components of a scanning electron microscope. (Source: https://fakultaeten.hu-berlin.de/en/mnf/forschung_internationales/grs/salsa/p-a-labs/application-lab/instrumentation/a-labs-sem).....	53
Figure 2.16. Various mechanisms of electron backscattering utilized by the ECCI method to generate contrast images. The image was acquired from [130]	54
Figure 2.17. ECCI image of GaAs epitaxially grown on GaP/Si substrate with a previous high TDD. The calculated TDD from the image is provided in the lower part, with yellow circles highlighting select some of TDs. It was adapted from reference [131]	55
Figure 2.18. (a) Kikuchi bands corresponding to Si(100). (b) Variation in band appearance upon rotating the structure by 10° and (c) tilting the structure by 10°. The arranged red spheres represent the unit cell and its altered orientation due to rotation and tilt. (Source: https://ssd.phys.strath.ac.uk/techniques/scanning-electron-microscopy/electron-backscatter-diffraction-ebbsd/)	56
Figure 2.19. (a) KAM map of a GaN thin film displaying dislocations. (b) ECCI image illustrating individual dislocations from (a). (Source: https://www.ebsd.com/ois-ebbsd-system/dislocation-density-analysis)	57
Figure 2.20. Custom-built setup for measuring EQE and reflectance at IES-UPM.	58
Figure 2.21. In-house setup for measuring dark and light I-V curves at IES-UPM.....	59
Figure 3.1. RAS spectra for both t-batch (a) and T-batch (b) during baking at 640°C. The purple arrow highlights the protruding signal around 3 eV.	65
Figure 3.2. Reflectance spectra for t-batch (a) and T-batch (b) during baking at 640°C.	66

Figure 3.3. RAS signal (transient mode) for both t-batch (a) and T-batch (b) samples during III-V deposition. The black dashed lines indicate the initiation of each stage of the epitaxy process.	67
Figure 3.4. Reflectance signal (transient mode) for t-batch (a) and T-batch (b) during III-V deposition. Vertical dashed lines denote the start of each epitaxy stage. The thick black arrow shows the correlation between valley positions and GR. The horizontal dotted line indicates a linear signal evolution with no observed drop-off.	69
Figure 3.5. KAM maps for the t-batch samples.....	71
Figure 3.6. KAM maps for the T-batch samples.	72
Figure 3.7. KAM maps for the sample with deposited Ge on standard Ge substrate (Ge/Ge)	73
Figure 3.8. The first row presents ADF-STEM images of samples t40 and t120, while the subsequent images are obtained via BF-TEM method. Yellow rectangles highlight defect-free regions, and yellow ellipses indicate misfit dislocations at the Ge Si interface. Blue arrows denote cracks reaching the Ge surface, and the red arrow indicates self-annihilated cracks.....	74
Figure 3.9. HRTEM images of the Ge Si interface illustrating the dislocations disrupting the atomic arrangement continuity (blue and green lines) due to significant lattice mismatch. Pink arrows indicate the characteristic 60° orientation of dislocations in Ge on Si, showing both possible orientations	75
Figure 3.10. ABF-STEM micrographs of Ge layers deposited on Ge substrates (Ge/Ge). (a) Yellow arrows highlight cracks extending from the Ge/Ge interface to the surface. (b) Magnified view of a region where sessile cracks are observed near the Ge/Ge interface, not extending to the surface	76

Figure 3.11. TEM micrographs (right) and corresponding representative AFM scans (left) for Epi-Sample (a) and Raw-Sample (b) 77

Figure 3.12. AFM images of Ge|Si samples before (left) and after (right) MOVPE thermal load..... 77

Figure 3.13. ADF-STEM images depicting the Ga(In)As/GaAs/Ge|Si structure for samples t40 and t20 (upper section) and a magnified ADF-TEM image for sample t120 (below section), illustrating the two interfaces. Green arrows indicate dislocations propagating from the Ge layer to the surface, while the yellow ellipse highlights misfit dislocations at the Ge|Si interface 78

Figure 3.14. ECCI images at two different magnifications for the t-batch samples, organized in columns. Yellow arrows indicate selected TDs for reference 80

Figure 3.15. AFM images ($2 \times 2 \mu\text{m}^2$) depicting selected t-batch samples. The accompanying profiles represent cross-sectional blue lines marked on the respective AFM images. The parameter d denotes the distance between the peaks of the surface features. Yellow arrows indicate the presence of TD 83

Figure 3.16. AFM images ($2 \times 2 \mu\text{m}^2$) depicting the T-batch samples. The profiles shown below the images represent cross-sectional blue lines marked on the corresponding AFM images. The parameter d indicates the distance between the peak lines, while yellow arrows indicate TD 84

Figure 4.1. RAS signatures during the nucleation of the GaInP layer on the Ge surface of a standard Ge (reference) substrate compared to GON-treated samples..... 91

Figure 4.2. EQE of TJSCs grown on standard Ge substrates and GON samples..... 92

Figure 4.3. Light and dark J-V characteristics for each GON sample compared to the reference sample (standard Ge substrate). (a) Comparison between F200 and the reference sample, (b) F1500 and the reference sample, (c) F5000 and the reference sample, and (d) dark I-V curves of all samples for direct comparison..... 93

Figure 4.4. (a) Transfer of III-V/Ge stack of the sample F1500 onto freestanding Kapton tape using manual methods. (b) Solar cells transferred in two stages onto Kapton tape affixed to a glass slide. The glass slide mitigated bending and cracking of the layers but resulted in reduced peeling pressure at the crack front, thus preventing complete detachment in the initial attempt..... 94

Figure 5.1. Vacancy mechanism for self-diffusion. The labeled Ge atom migrates by jumping to the vacancy to its right once the value of H_m is exceeded. The green spheres represent Ge atoms and the blue circles represent vacancies..... 99

Figure 5.2. Graphical representation of simulations featuring different concentration dependencies. Profiles of donor concentrations depicted by colored lines representing different diffusion scenarios: constant diffusivity (blue), linear concentration-dependent diffusivity (red), quadratic concentration dependence (green), and cubic concentration dependence (magenta). The arrow direction indicates the trend of a more abrupt drop-off in profile 101

Figure 5.3. Schematic depiction of the ring mechanism of diffusion in the Ge lattice. The diagram features a black sphere representing a single donor, a green square representing V_{Ge} and green spheres portraying the Ge atoms. This representation was sourced from [164] 105

Figure 5.4. Schematic representation of the cross-diffusion mechanism. Ge atoms are represented by green spheres, Ga atoms by red spheres, As atoms by yellow spheres, and vacancies in each layer by white circles. The left image depicts the initial state of the two adjacent layers, while the right image illustrates how atoms diffuse into their corresponding adjacent layers. The choice of GaAs is purely illustrative, as this mechanism can occur for other layers as well. 107

Figure 5.5. Target structure for Ge SJSC at IES-UPM. 108

Figure 5.6. Schematic graph of the temperature profile in a GaAs deposition on Ge depicting the five stages of the process. Simplified illustrations of every stage are pictured. The time axis is not to scale..... 110

Figure 5.7. RMS roughness vs preexposure times. The RMS roughness obtained from different AFM scan areas is included (see Figure 5.8). The RMS values for $2 \times 2 \mu\text{m}^2$ areas include standard deviation (σ_{STD} ; represented by bars) whilst $5 \times 5 \mu\text{m}^2$ and $10 \times 10 \mu\text{m}^2$ scans were measured once..... 111

Figure 5.8. In the right column, AFM images of $5 \times 5 \mu\text{m}^2$ for each preexposure time, while the left column showcases one-dimensional profiles of the surfaces derived from the corresponding AFM images..... 113

Figure 5.9. ECV profiles for the samples with 50-nm GaAs and variable AsH_3 preexposure times (colored numbers). A simple illustration of the structure is placed in the lower left corner. The shaded region in black tags the p-type influence exerted by Ga on the prevailing n-type profile..... 114

Figure 5.10. Concentration profiles obtained from SIMS measurements (empty circles) and ECV profiles (filled circles) for samples exclusively exposed to AsH_3 . The y-axis denotes the arsenic concentration, labeled as As, aligning with SIMS measurements, while the electron concentration from ECV measurements is denoted as e^- 115

Figure 5.11. SIMS profiles for samples with AsH_3 preexposure times of 1 s (black circles) and 15 s (black squares). Simulations, depicting a linear concentration dependence, are overlaid on the experimental data. The blue line corresponds to the simulation for the 1-s profile, while the red line represents the 15-s profile simulation..... 116

Figure 5.12. SIMS profiles illustrating As distribution in samples with varying GaAs thicknesses and a consistent preexposure time of 20 seconds. Profiles corresponding to GaAs deposition times of $t_{GaAs} = 20$ s (blue), $t_{GaAs} = 120$ s (green), and $t_{GaAs} = 240$ s (black) are depicted. Additionally, a sample subjected solely to AsH₃ preexposure for 15 seconds (red) is included to directly observe the evolution of As diffusion..... 118

Figure 5.13. Profiles of As determined by SIMS for various growth conditions. Filled circles represent profiles of samples exposed to AsH₃ for 1 s (red) and 15 s (red). Upward triangles indicate samples with $t_{GaAs} = 240$ s, with different preexposure times of 1 s (green) and 20 s (blue)..... 119

Figure 5.14. SIMS profiles depicted with black and red markers alongside simulated profiles using a linear dependence in concentration (blue lines). The blue solid line corresponds to the simulation based on the experimental data for the sample exposed to AsH₃ for 15 seconds (black squares). Additionally, a profile with an extra 20 seconds (blue dashed line) beyond the blue solid profile is presented. The blue dotted line illustrates another simulated profile, requiring approximately 15 times the duration (from the blue dashed profile) to match with the red profile 120

Figure 5.15. SIMS profiles depicting samples with a constant AsH₃ preexposure time of 20 seconds and varying GaAs deposition durations. The purple shaded area denotes that the boundary conditions for simulation are, on average, 1.5 times higher than the reference value U_0^{Ref} [180]..... 121

Figure 5.16. SIMS profiles illustrating the diffusion characteristics of samples subjected to various treatments: (1) AsH₃ preexposure for 15 seconds (black circles), (2) 20 seconds of preexposure followed by 20 seconds of GaAs deposition (black triangles), and (3) 20 seconds of preexposure followed by 240 seconds of GaAs deposition (black squares). The colored solid lines depict simulations based on linearly dependent diffusivity in concentration. Dotted lines indicate the profiles right before the initiation of the cooldown stage (As-grown) 122

Figure A.1. Spatial (i) and time (j) discretization schematic. Δx and Δt denote spatial and time intervals. Red points connected by blue lines to calculate U_i^{j+1} 133

Figure A.2. Newton-Raphson's method extrapolates the local derivative to find the next estimate of the root. 135

Figure A.3. Graphical representation of the (second-order) Runge-Kutta method. The blue lines depict the extension from t to $t + \Delta t$ with a slope determined by Euler's method (indicated with *). The green line represents the subsequent step of the method, where a new slope obtained at $t + \frac{1}{2}\Delta t$ provides a more accurate approximation for the red curve..... 139

Figure A.4. Resultant simulations following the parameters indicated in Table V.I for constant diffusivity (dash-dotted line) and linearly concentration-dependent diffusivity (solid line). For these simulations, the value of L is $0.5 \mu\text{m}$ 144

List of Tables

Table I.I. TEC values for various materials. The values for Si and GaAs were sourced from [43] while the TEC value for GaP is referenced from [15]	11
Table I.II. Solar cell parameters for two types of multijunction solar cells. On the left side, parameters for triple junction solar cells are listed, while on the right side, parameters for double junction solar cells are provided. The respective structures are indicated in the heading cells for easy reference	13
Table I.III. TEC values for a range of materials. The TEC values for Si, Ge and GaAs were obtained from [43], whereas the TEC value for $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ is cited from [55]	14
Table I.IV. Solar cell parameters for various configurations utilizing Ge Si virtual substrates. Parameters for single-junction solar cells are listed on the left side, while those for double-junction solar cells are provided in the middle. Additionally, parameters for triple-junction solar cells are indicated on the right side. The corresponding structures are specified in the heading cells for convenient reference.....	17
Table III.I. Growth parameters for the batch of different ultra-thin Ge thickness	63
Table III.II. Growth parameters for the batch of different temperatures	63
Table III.III. Values of TDD for the t-batch.....	79
Table III.IV. Values of RMS roughness for the t-batch	81
Table III.V. Values of RMS roughness for the T-batch.....	82

Table V.I. Pre-exponential factor and activation energy values of the group III elements in Ge. The documented values for Al, Ga, and In can be found in [165] for aluminum, [166] for gallium, and [167] for indium..... 103

Table V.II. Pre-exponential factor and activation energy values pertaining to As diffusion in Ge. The corresponding values are referenced as follows: linear concentration-dependent diffusivity in [180], quadratic dependence in [182] and cubic dependence in [162]. The symbol m signifies the charge state of the vacancies..... 106

Table V.III. tabulated values of D_0 and U_0 for As diffusion simulations, comparing results from the reference literature with profiles obtained after AsH_3 preexposure times of 1 s and 15 s. Relative errors ($\epsilon_{rel}^{D_0}$) are provided for comparisons with the reference value of D_0 117

Table A.I. Arbitrary values of activation energy and the pre-exponential factor for the two selected examples, with resultant simulations presented in Figure A.4. Superscripts 0 and 1- indicate parameters for the vacancy state of charges in a neutral or single negative state, respectively. The explanation of this can be read in Section 4.1..... 144

List of Abbreviations and Acronyms

ABF	Annular bright field
ADF	Annular dark field
AFM	Atomic force microscope
APD	Anti-phase domain
ARC	Anto-reflection coating
BF	Bright field
CED	Cumulative energy demand
CGB	Compositionally graded buffer
CVD	Chemical vapor deposition
DC	Direct current
DETe	Diethyl telluride
DF	Dark field
DJSC	Double junction solar cell
DMZn	Dimethyl zinc
DTBSi	Di-tert-butylsilane
EBSD	Electron backscatter diffraction
ECCI	Electron channeling contrast imaging
ECV	Electrochemical capacitance-voltage
EQE	External quantum efficiency
FF	Fill factor
GON	Germanium on nothing
GR	Growth rate
HRTEM	High-resolution transmission electron microscopy
IES-UPM	Instituto de energía solar – Universidad politécnica de Madrid
IMM	Inverted metamorphic multijunction
IQE	Internal quantum efficiency

IR	Infrared
KAM	Kernel average misorientation
LEED	Low-energy electron diffraction
MBE	Molecular beam epitaxy
MJSC	Multijunction solar cell
MOVPE	Metal organic vapor phase epitaxy
PDE	Partial differential equation
PV	Photovoltaics
RA	Reflectance anisotropy
RAS	Reflectance anisotropy spectroscopy
RF	Radio frequency
RF-PECVD	Radio frequency plasma enhanced chemical vapor epitaxy
RMS	Root mean square
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectrometry
SJSC	Single junction solar cell
SR	Spectral response
STM	Scanning tunneling microscopy
TD	Threading dislocation
TDD	Threading dislocation density
TEC	Thermal expansion coefficient
TEM	Transmission electron microscopy
TJSC	Triple junction solar cell
TMAI	Trimethyl aluminum
TMGa	Trimethyl gallium
TMIn	Trimethyl indium
TPV	Thermophotovoltaics
UV	Ultraviolet

List of Symbols

α	Thermal expansion coefficient / Angle of incidence of the light
ΔE_{AV}^f	Binding enthalpy of a donor/vacancy pair
$\varepsilon_{rel}^{D_0}$	Relative error for simulation D_0 and D_0 from the corresponding reference
η_{eff}	Efficiency
λ	Wavelength
μ_n	Electron mobility
μ_p	Hole mobility
σ_{STD}	Standard deviation
τ	Lifetime
τ_0	Minority carrier lifetime without TDD
τ_n	Electron lifetime
τ_p	Hole lifetime
τ_{TDD}	TDD-limited minority carrier lifetime
Φ	Spectral irradiance
A	Area
A_s	Substitutional donor
A_s^r	Substitutional donor with positive charge r
AV	Donor/vacancy pair
B	Radiative recombination coefficient
C	Capacitance
C_v^{eq}	Equilibrium concentration relative to Ge atomic density
$C-V$	Capacitance-voltage
d	Layer thickness / Separation among rooftop-like shapes
D	Diffusion coefficient or diffusivity
D_0	Pre-exponential factor
D_0^I	Pre-exponential factor of interstitial

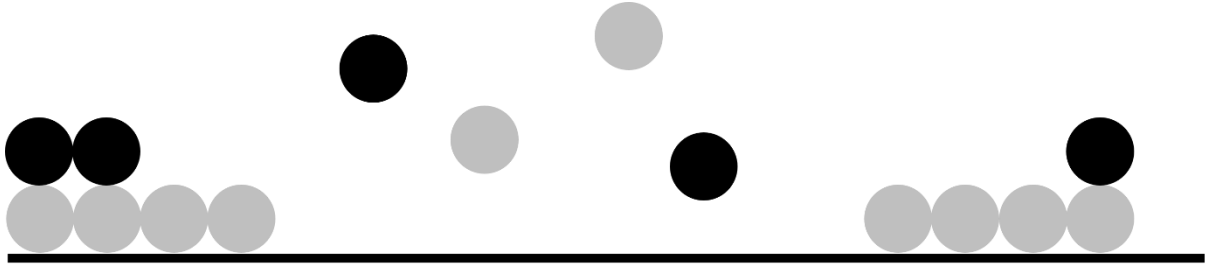
D_0^m	Pre-exponential factor for As diffusion in Ge with negatively charged vacancy m
D_0^V	Pre-exponential factor of vacancy
D_{Ge}^0	Diffusion coefficient of the vacancy in Ge with no charge
D_{Ge}^{m-}	Diffusion coefficient of the vacancy in Ge with negative charge m
D_{Ge}^{s+}	Diffusion coefficient of the vacancy in Ge with positive charge s
d_{max}	Maximum layer thickness in Fabry-Perot oscillations
d_{min}	Minimum layer thickness in Fabry-Perot oscillations
D_n	Electron diffusion coefficient
D_p	Hole diffusion coefficient
D_V	Diffusion coefficient of the monovacancy in Ge
E	Photon energy
E_a	Activation energy
E_a^I	Activation energy of interstitials
E_a^V	Activation energy of vacancies
f_V	Correlation factor
Ge/Ge	Germanium deposited on germanium
Ge Si	Germanium on silicon
GeSi	Germanium and silicon alloy
H_{AV}^f	Formation enthalpy of a donor/vacancy pair
H_F	Enthalpy of formation
H_m	Enthalpy of migration
H_V^f	Formation enthalpy of an isolated vacancy
I	Current / Interstitial
I_{sc}	Short-circuit current
$I-V$	Current-voltage
J	Current density
J_0	Saturation current density
J_L	Photogenerated current density

J_{sc}	Short-circuit current density
J - V	Current density-voltage
m	Order of interference / Negative value of the vacancy charge in absolute value
n	Electron concentration / Referred to electrons
N	Carrier concentration
N_A	Concentration of acceptors
N_D	Concentration of donors
N_{Dopant}	Concentration of dopants
n_i	Intrinsic carrier density
N_{TDD}	Value of density of threading dislocations
p	Hole concentration / Referred to holes
Q	Charge
r	Reflectance / Positive charge of the substitutional donor
R	Reflectance
s	Positive value of the vacancy charge
T	Temperature
t_{GaAs}	Deposition time of GaAs
t_{preexp}	AsH ₃ preexposure time
U	Generic concentration
U_0	Value of the infinite source
U_0^{Ref}	Value of the infinite source in the corresponding reference
V	Voltage / Vacancy
V^-	Vacancy with singly negative charge
V^{2-}	Vacancy with double negative charge
V^{3-}	Vacancy with triple negative charge
V_{Ge}	Germanium vacancy
V_{Ge}^m	Germanium vacancy with negative charge m
V_{oc}	Open-circuit voltage

W Width of the depletion region

List of constants

ε_0	Dielectric constant in the vacuum
ε_r	Relative dielectric constant
c	Light speed
h	Planck constant
k_B	Boltzmann constant
q	Electron charge



Introduction

CHAPTER 1

1.1 Motivation

1.1.1 Global warming

The observed increase in global temperatures over recent decades is well-documented [1]. This concerning trend is largely attributed to the substantial contribution of fossil fuels (oil, gas and coal) to the emission of gases, such as CO₂, into the atmosphere, thereby inducing the greenhouse effect. As a consequence, sunlight penetrates the Earth's atmosphere, reaching the surface where it is absorbed and re-emitted as IR radiation. This emitted heat, then, is absorbed again by the greenhouse gasses, leading to the re-radiation into the ground. Therefore, the average global temperature is on alarming ascent, as depicted in Figure 1.1. This graph utilizes the global temperature relative to an average between 1961 and 1990 as a reference point and reveals an average rise exceeding 0.8 °C since then.

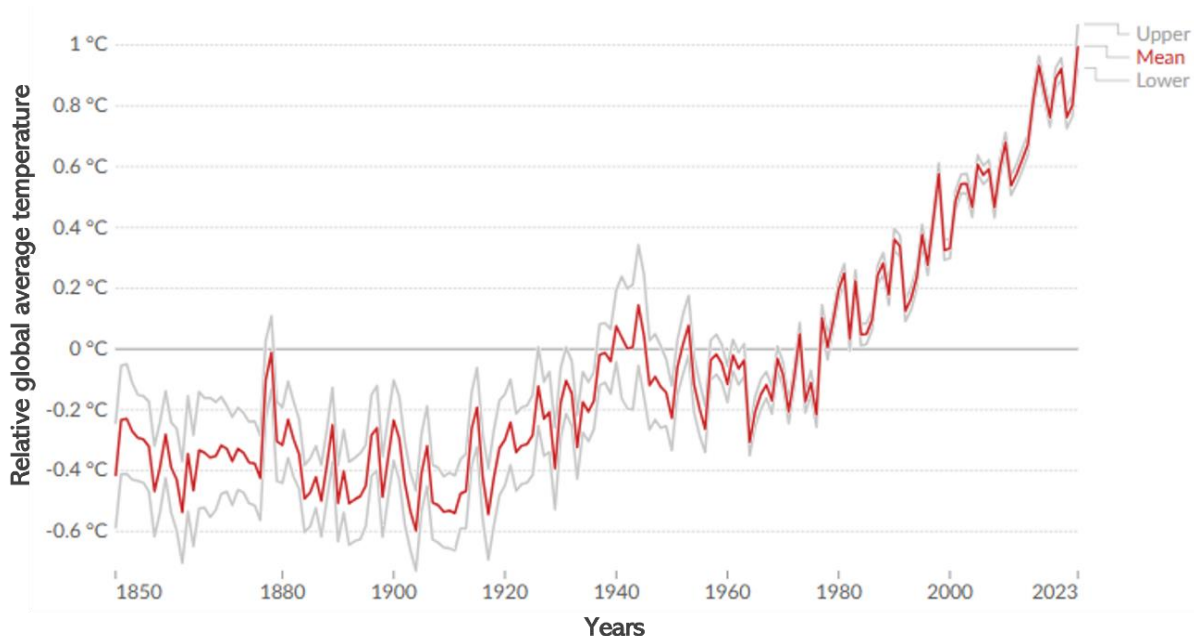


Figure 1.1. Temporal trends in global mean temperature from 1850 onward. The red line represents the mean temperature, while the surrounding grey lines delineate the upper and lower bounds of the 95% confidence intervals. Source: <https://ourworldindata.org/co2-and-greenhouse-gas-emissions>.

Global CO₂ emissions represent the primary driver of the current greenhouse effect concerns. Despite a temporary 5.5% reduction in global CO₂ emissions in 2020 due to the COVID-19 pandemic, projections indicate a 1.1% increase in emission by 2023. That means that, since 1990, global CO₂ emissions have increased by more than 60 %. In 2022, coal contributed 40.7%, oil 31.3%, gas 21.5% and other sources 6.5% to total emissions (source: <https://ourworldindata.org/emissions-by-fuel>).

The consequences of climate change are manifest and extensively studied. Changes in atmospheric dynamics have resulted in an increased frequency of storms [2], leading to intense rainfalls, flooding and costly material damage. On the other hand, drought poses another significant problematic [3] whose repercussion is a severe lack of water for both irrigation crops and human consumption. Figure 1.2 shows a photograph of the Lake Powell (Arizona and Utah) where the impact of the droughts on the available volume of water is noticeable. Furthermore, global warming is linked to the loss of species [4]. Biodiversity tends to decline over time, what it entails a loss of important biological information.

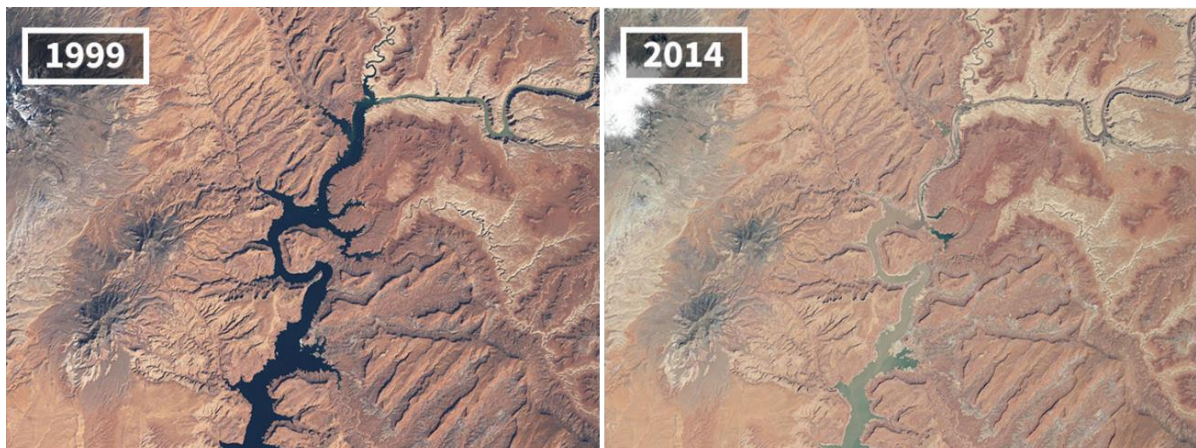


Figure 1.2. Comparative images depicting Lake Powell (Arizona and Utah) in 1999 (left) and 2014 (right), illustrating the impact of prolonged drought conditions. Source: <https://climate.nasa.gov/images-of-change>.

The promotion of clean energies (e.g. solar and wind energy) offers a viable solution to mitigate the reliance on fossil fuels, like coal, in power generation [5] and shift towards cleaner energy sources to alleviate the impact of global warming [6]. Fortunately, there is a growing awareness of this issue, and some policies have already been implemented. The European Union (UE), for instance, has taken a leadership role in climate action, with a commitment to reducing greenhouse gas emission and achieving carbon neutrality by 2050 (source: <https://climate.ec.europa.eu>). Additionally, several countries are developing plans to encourage the use of renewable energies. *El Plan Nacional Integrado de Energía y Clima (PNIEC)* foresees a significant increase of renewable energies in Spain, aiming for 74% of energy consumption to be sourced from clean energy. An estimated investment of €3165 million is allocated for this purpose. (source: <https://planderecuperacion.gob.es/politicas-y-componentes/componente-7-despliegue-e-integracion-de-energias-renovables>).

1.1.2 Solar energy as solution

The utilization of fossil fuels not only contributes to global warming but is also constrained by the finite nature of its resources. In recent decades, there has been a rising concern regarding the irreversible decline in oil production, often referred to as *peak oil*, once its maximum rate is reached. Some authors argue that this critical point may have already been surpassed [7], [8], whereas others contend that it is yet to occur [9]. Despite these divergent viewpoints, a consensus exists among scholars that if the current rate of consumption persists, as documented in [10], [11], both our lifestyle and the sustainability of economic and developmental endeavors will become untenable.

In an effort to mitigate greenhouse gas emission and reduce dependence on fossil fuels, solar energy has emerged as a promising alternative. PV involves the collection of sunlight for its conversion into electricity. Extensive research has been conducted to explore the potential of PV systems. Across vast expanses, PV technology can effectively supply electricity to a numerous urban areas, especially when power-generating solar units are strategically located in conjunction with auxiliary Diesel systems [12]. Distributed small-scale PV systems, rather than large solar plants, offer not only energy supply but also present lucrative opportunities for investors [13], instilling confidence in sustainable green energy systems. Furthermore, maximizing the efficiency of a PV system through advanced storage technologies enhances its overall effectiveness [14].

The main advantage of the solar energy lies in its function as a practically infinite source. The radiation emitted by the Sun can be characterized through the solar spectrum, which represents the incoming energy reaching the Earth and spans a range of electromagnetic radiation from UV to IR region. This spectrum is comprised of photons with diverse wavelengths, defining the spectrum's shape and intensity. However, these characteristics can be altered as solar radiation traverses the atmosphere. Upon reaching the Earth's surface, the solar spectrum undergoes modifications compared to its pre-atmospheric crossing state, as illustrated in Figure 1.3. The red line in the Figure corresponds to the AM0 spectrum, devoid of atmospheric effects, while the blue line represents the AM1.5G spectrum, measured on earth surface. In this spectrum, different valleys are observed, associated with absorption bands of H₂O, O₂ and CO₂. Consequently, solar cell designs for terrestrial applications must contemplate these atmospheric influences.

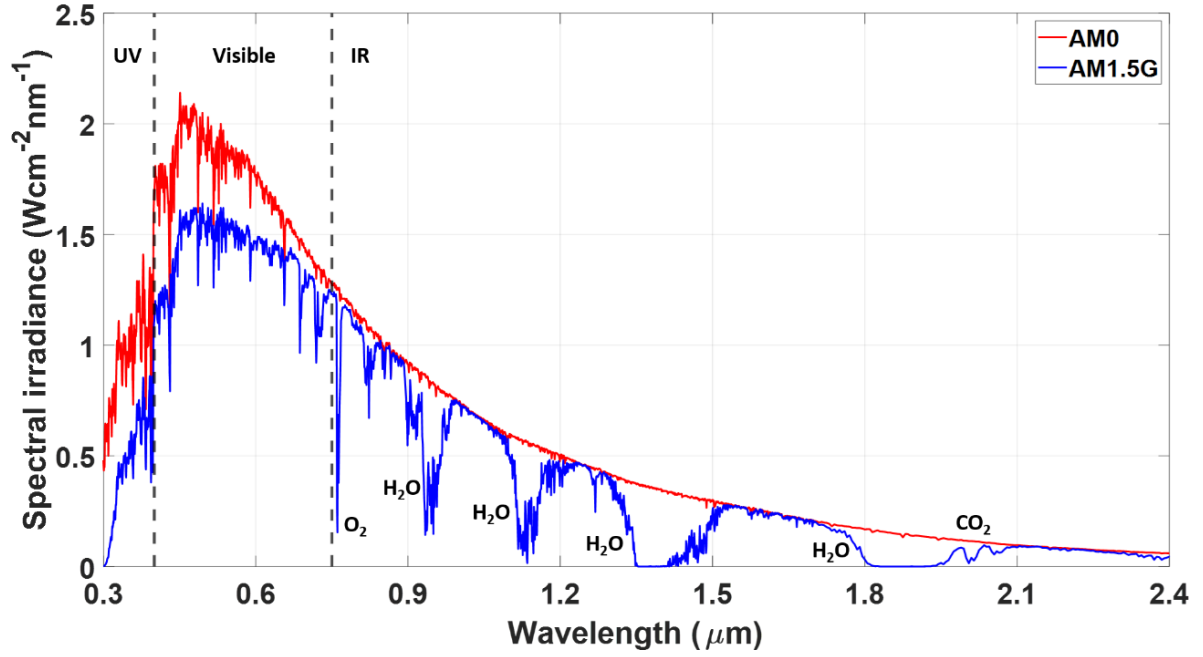


Figure 1.3. Graph of the irradiance for solar spectra AM0 (red) and AM1.5G (blue). Spectra are divided into three ranges: UV, visible and IR. Tag positioned adjacent to blue valleys denote the absorption bands for specific molecules in the atmosphere.

The spectral photon energy associated with this phenomenon can be collected by channeling it through a material. In essence for semiconductor materials, the orderly arrangement of a big number of atoms (as those in a solid) gives rise to two different continuous bands. Figure 1.4. shows a schematic representation of these bands. The lower band, or valence band, represents a continuous state where negatively charged electrons are weakly bound to their positively charged nuclei. The upper band, known as the conduction band, represents a continuous state which allows electrons to move freely. These bands are energetically separated by the so-called energy gap or bandgap. An electron can promote from the valence bands to the conduction band with the absorption of a certain quantity of energy. As a consequence, this transition results in the generation of a positively charged hole within the valence band. The energy required for the electron transition is at least equal to the bandgap and is directly related to the wavelength of the incident photon, as described by Eq. 1.1:

$$E = \frac{hc}{\lambda} \quad (\text{Eq. 1.1})$$

Thus, the bandgap value determines the portion of the solar spectrum that a semiconductor can absorb. Photons with wavelengths shorter than the bandgap are absorbed, while those with longer wavelengths pass through the semiconductor without absorption. For instance, at 300 K, the bandgaps for typical semiconductors such as Si, Ge and GaAs are 1.14 eV, 0.67 eV and 1.43 eV, respectively [15]. This corresponds to wavelengths values of 1090 nm, 1850 nm

and 870 nm. Wavelengths exceeding these values are not absorbed, rendering the semiconductor transparent to them.

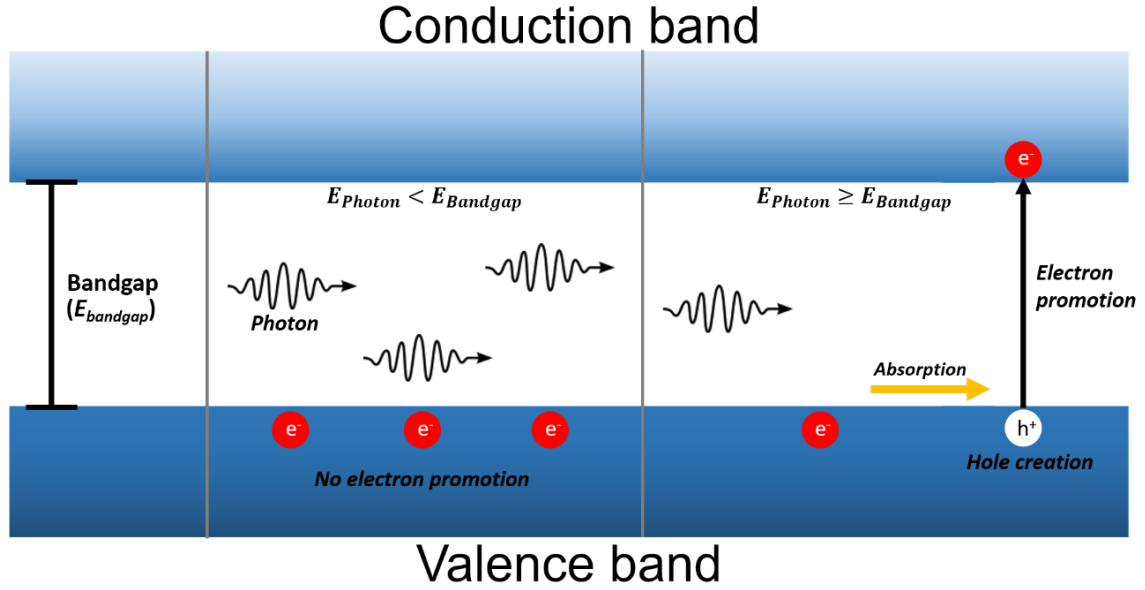


Figure 1.4. Band diagram of a semiconductor. When the energy photon is below the bandgap, electrons remain in the valence band (below) without promotion to the conduction bandgap (top). Conversely, photon energies exceeding the bandgap permit electron promotion, creating a hole in the valence band where the electron was originally located.

As explained above, semiconductors absorb specific wavelength ranges depending on their bandgap. Consequently, our focus briefly shifts to the SR. Defined as the ratio of the current generated by the solar cell to the power incident upon it. SR is connected to IQE through the following expression:

$$SR(\lambda) = \frac{q\lambda}{hc} \cdot (1 - R(\lambda)) \cdot IQE(\lambda) \quad (Eq. 1.2)$$

Given that IQE is directly proportional to the material's absorbance, SR is inherently sensitive to the bandgap of the material. This parameter will serve a visual purpose in future Figures, particularly multiplying SR by the spectral irradiance. This product quantifies the current generated per wavelength and unit area, offering insights into the absorbance characteristics of various semiconductors and lightly enhancing the understanding of their applications in electronics.

1.2 Semiconductors in electronics and solar energy

1.2.1 Silicon technology

Since the inception of the first silicon-based transistor was manufactured in the 1950's [16], there has been continual progression of research and applications, marking some advancements in the field [17]. Si stands out as a widely employed material with varied

applications encompassing the semiconductor and electronics industry [18]. A pivotal factor underpinning the extensive use of Si is its abundant presence in the Earth's crust [19]. This abundance has facilitated rapid progress, leading to the miniaturization of Si devices down to the micro and nano scales [20]. Hence, the downsizing of Si-based devices to these smaller scales has resulted in a notable reduction in material consumption. This reduction has been instrumental in driving a gradual decrease in costs over time [17]. The efficiency gains achieved through downsizing, coupled with the inherent abundance of Si, have collectively contributed to the economic viability and sustainability of Si-based technologies.

Notably, Si has long been the predominant semiconductor in PV applications [21], [22]. However, it is facing challenges as it approaches its efficiency limits. The theoretical efficiency limit in Si solar cells has been established at approximately 32 % [23], [24], yet recent research endeavors have yielded an efficiency of 27.6 % [25]. This slight discrepancy underscores the upcoming limitation of efficiency in Si-based photovoltaics. The pursuit of advanced Si-based technologies capable of pushing the efficiency is confronted with the necessity for substantial investments in research, development, and manufacturing infrastructure. The escalating costs associated with pushing these efficiency limits pose an economic riddle, prompting a critical evaluation of the sustainability of further improving silicon's efficiency without venturing into alternative materials or innovative approaches. The dynamic landscape of semiconductor research is witnessing a shift towards exploring new materials and methodologies that can surmount the inherent constraints of Si.

1.2.2 Ge and III-V high efficiency technology

Ge plays a multifaceted role in modern electronics, demonstrating versatile applications across various domains. Its principal advantage lies in its capacity to absorb a broad range of IR photon energies. In the realm of IR photodetectors, germanium's unique properties make it an ideal material [26]. Its sensitivity to IR radiation enables efficient detection in applications such as remote sensing technologies [27]. Moving beyond photodetectors, Ge occupies a prominence position in the development of high-speed electronic devices. Its intrinsic properties, including a high electron mobility, render it well-suited for applications demanding rapid signal response. Germanium-based transistors [28] and diodes [29] contribute to the design of high-speed electronic circuits, facilitating advancements in telecommunications and data processing technologies.

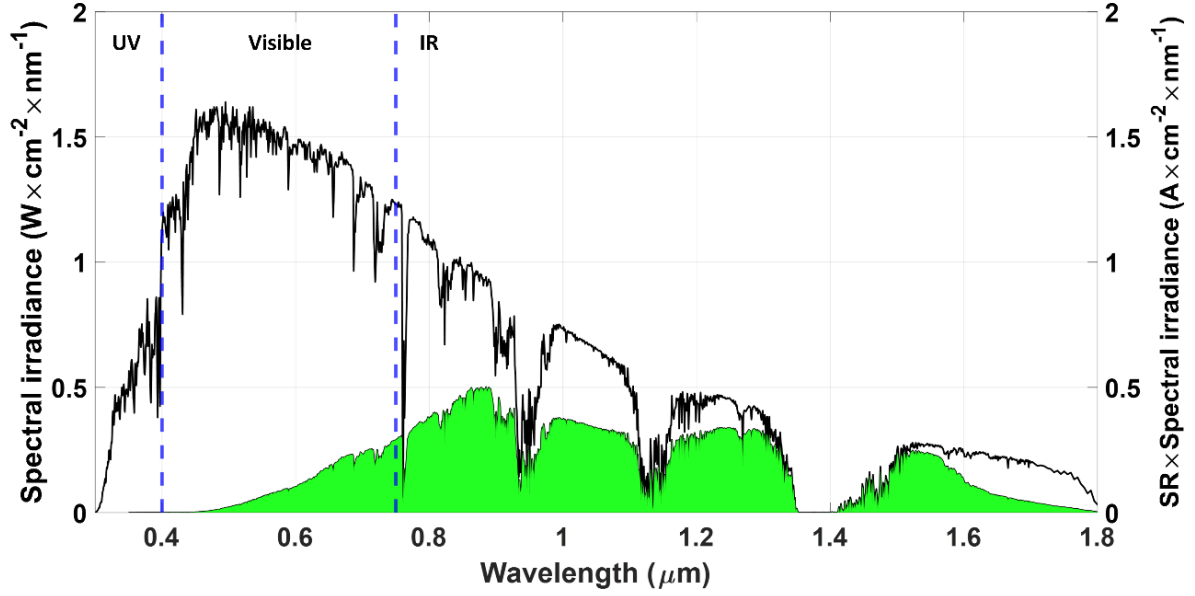
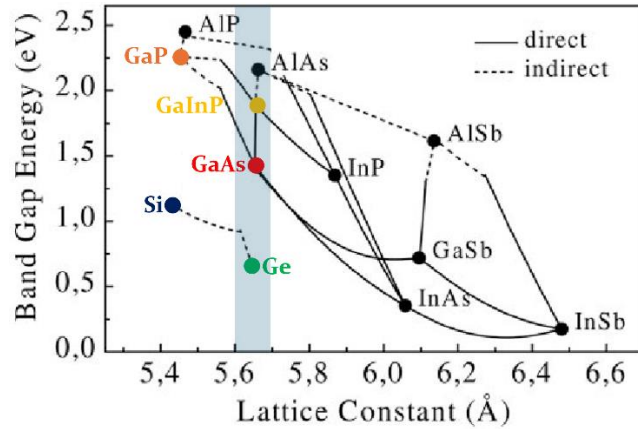


Figure 1.5. Graph of the irradiance for solar spectra AM1.5G (black line). Spectra are divided into three ranges: UV, visible and IR. The green-shaded spectrum area indicates the product of SR and the spectral irradiance in a typical Ge solar cell.

In the field of PV, Ge assumes a crucial role, albeit with different characteristics compared to traditional Si. Ge solar cells [30], while less common, exhibit advantages in specific applications. With a narrower bandgap of 0.67 eV compared to silicon's 1.14 eV, Ge solar cells can collect a broader spectrum of sunlight into the infrared, as depicted in Figure 1.5. The green shaded area in a typical Ge single junction illustrates this capability through the product of SR and solar irradiance. This attribute proves advantageous in TPV. In TPV applications, molten materials emit irradiance predominantly within the IR spectrum, and Ge has been demonstrated to collect this radiation, as evidenced by the reliability in previous studies [31], [32]. However, this advantage is not applicable in conventional solar applications, necessitating the exploration of alternative materials.

III-V materials, compounds comprising elements from groups III and V of the periodic table, have emerged as this alternative material, showing versatility in various applications. This versatility stems from the wide possibilities of binary semiconductors, such as GaAs, InP or GaP, as well as ternary combinations (or higher) with tunable content like $\text{Ga}_x\text{In}_{1-x}\text{P}$, $\text{GaAs}_x\text{P}_{1-x}$ or $\text{Al}_x\text{Ga}_{1-x}\text{As}$. These diverse combinations offer an ample range of bandgaps (ranging 0.7 eV to 2.5 eV, as plotted in Figure 1.6) for many possible applications. III-V materials have also demonstrated exceptional potential in PV. GaAs [33] and other III-V compounds [34] are employed in space applications and concentrators solar cells [35], where their high efficiency in converting sunlight into electrical power is advantageous for both satellite and terrestrial applications.

Figure 1.6. Graph depicting the relationship between bandgap and lattice constant of III-V materials. The shaded area highlights semiconductors with similar lattice parameters, prevalent in typical electronics applications like PV.



The integration of III-V materials with Ge in solar cells represents a frontier of research and innovation, harnessing the complementary properties of these semiconductor materials (see next section). Historically, the integration of GaAs on Ge substrates has addressed challenges related to the production of cost-effective and high-efficiency solar cells [36]. However, in this design, featuring a maximum of two active layers, while efficient, leaves room for improvement. Enhancing efficiency is achievable through the incorporation of additional III-V layers, exemplified by the GaInP/GaInAs/Ge TJSC [37]. These tandem solar cell designs introduce the possibility for high-bandgap layers positioned above to permit longer wavelengths to pass through to layers below. Figure 1.7 sketches this phenomenon for the typical GaInP/GaInAs/Ge TJSC, indicating the product of SR and solar irradiance provided by the three active layers and a diagram elucidating how wavelengths are collected as they traverse each layer.

The utilization of Ge and III-V semiconductor technologies in various applications, including electronics and, specially, photovoltaics, is undeniably advantageous due to their superior electronic properties and potential for high-performance devices. However, it is crucial to acknowledge that both Ge and III-V technologies come with inherent cost challenges that have limited their widespread adoption. The expense associated with Ge technologies arises from factors such as the complex fabrication processes involved in obtaining high-quality Ge wafers and the overall scarcity of Ge [38]. On the other hand, III-V semiconductors present challenges related to the cost of raw materials, epitaxial growth, and intricate manufacturing techniques. Despite their remarkable properties, the high production and processing costs of Ge and III-V technologies have been a hindrance to their large-scale commercialization and have prompted research efforts to explore cost-effective alternatives and fabrication methods in order to make these technologies more economically viable for broader applications. In advance, a promising solution to mitigate the cost challenges associated with Ge and III-V semiconductor technologies is the utilization of Si as a template. Si serves as a substrate for the epitaxial growth of III-V materials, allowing for more economical fabrication processes.

This hybrid approach exploits the low cost of Si while preserving the superior electronic properties and efficiency of III-V semiconductors.

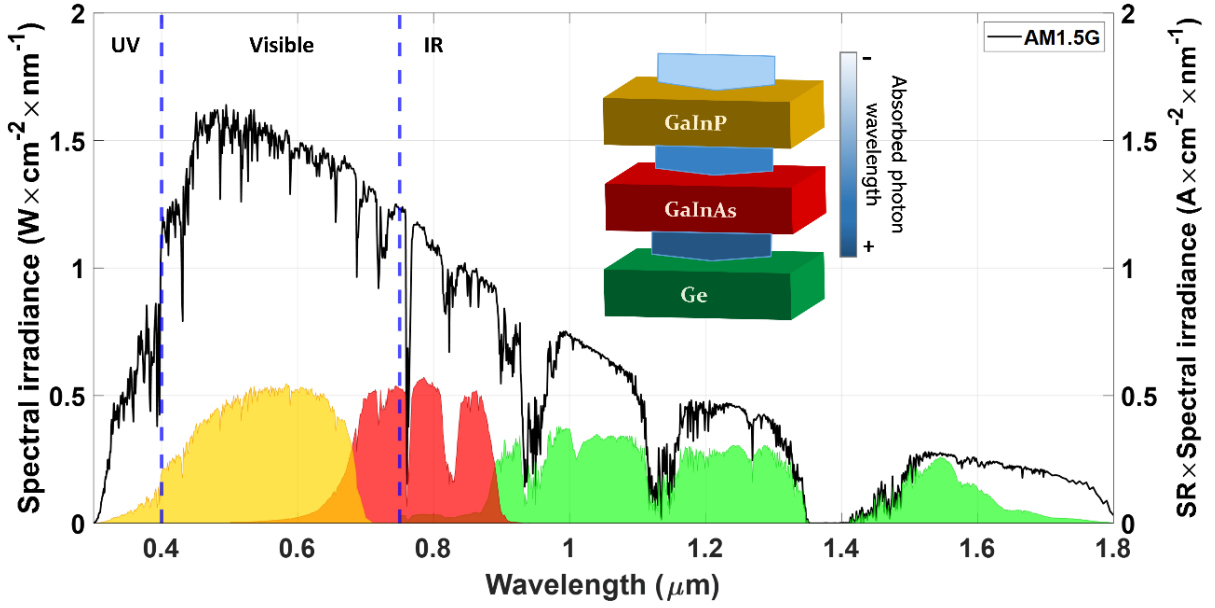


Figure 1.7. Graph of the spectral irradiance for solar spectra AM1.5G (black line). Spectra are divided into three ranges: UV, visible and IR. Shaded areas represent the product of SR and the spectral irradiance for each layer, in this case, the GaInP/GaInAs/Ge TJSC.

1.2.3 Integration of Si and III-V/Ge

The integration of III-V materials with Si in electronic devices has been a subject of research due to the unique properties offered by the already-mentioned III-V semiconductors. Overcoming historical challenges stemming from the lattice mismatch ($\sim 4.1\%$) between III-V materials and Si, and the growth of a polar on no-polar semiconductor have been the focal points. Techniques such as MBE and MOVPE have been employed to try to tackle these challenges. These integration technologies have been pivotal in realizing III-V/Si hybrid structures for various applications, ranging from high-speed electronic devices to optoelectronics [39], [40].

The integration of III-V semiconductors on Si substrates has garnered significant attention in PV due to the different advantages it offers. One notable advantage is the potential for cost reduction achieved through the use of Si as a template instead of directly employing III-V materials such as GaAs. This hybrid approach takes advantage of the best features of both Si and III-V materials, enabling the creation of high-performance yet cost-efficient photovoltaic devices.

III-V/Si solar cells have found applications in high-efficiency photovoltaic devices. III-V/Si solar cells have demonstrated good performance. However, a significant challenge in their practical

implementation is the emergence of TD, which can degrade the device's performance [41]. In the multi-junction context, III-V/Si tandem solar cells have showcased the potential to achieve even higher efficiencies by stacking multiple layers of semiconductors [34]. Despite the advancements, addressing the issue of TD remains a critical concern for optimizing the performance of III-V/Si solar cells. In the next sections the main technologies used for the integration of III-V on silicon for PV are reviewed. We only pay attention to the technologies enabling a monolithic integration.

1.2.3.1 GaP/Si technology

The use of GaP as a buffer layer in depositing III-V semiconductors on Si for PV applications has gained attention. The lattice compatibility of GaP with Si is evident from Figure 1.6, demonstrating close alignment between the lattice parameters of GaP and Si, which significantly reduces the occurrence of misfit dislocations in this nucleation layer. Furthermore, the wide bandgap of GaP offers advantages for PV applications, mitigating undesired light absorption. GaP serves as a nucleation layer, as sketched in Figure 1.8(a), facilitating epitaxy by providing a smooth, uniform surface onto which the desired material can be deposited with high quality and minimal defects.

Tandem solar cells, such as the GaAs/GaP/Si configuration, highlight the significance of GaP nucleation layers in photovoltaic applications [42]. One of the primary challenges faced in such configurations is the substantial lattice mismatch between GaP and GaAs-based materials, again referred to Figure 1.6. Additionally, TEC, denoted by α_{TEC} , disparities pose concerns during growth. Table I.I shows TEC values for Si, GaP and GaAs revealing a α_{TEC}^{Si} approximately half as low as the other two materials. This difference poses a significant challenge in high-temperature growth techniques, particularly during the gradual cooldown phase. In this context, the varying rates of contraction between different materials give rise to a dynamic alteration of lattice constants (or lattice mismatch). This dynamic change can lead to the emergence of cracks as will be shown later.

	Si	GaP	GaAs
$\alpha_{TEC} (10^{-6} K^{-1})$	2.6	4.89	5.7

Table I.I. TEC values for various materials. The values for Si and GaAs were sourced from [43] while the TEC value for GaP is referenced from [15].

To tackle this challenge, dislocation filters have been employed. Essentially, these layers serve a dual purpose: first, they act as a reservoir, effectively trapping potential TD arising from the GaP/Si substrate, owing to their substantial thickness. Secondly, this spatial allowance within the layer promotes the self-annihilation of migrating TDs upon encountering one another, a

phenomenon schematized in Figure 1.8(a). As an example of this approach, researchers have utilized a GaAs dislocation filter on GaP/Si substrates [44] to capture TD originating from misfit dislocations in the GaAs layer. Nonetheless, incorporating dislocation filter layers introduces additional material expenses and does not guarantee a sufficiently low TDD to avoid impacting the final PV efficiency [45]. Alternatively, another epitaxial approach has been developed utilizing GaAsP-based buffer layers, which demonstrate enhanced tolerance to defects and threading dislocations. This is achieved through the implementation of a graded $\text{GaAs}_x\text{P}_{1-x}$ buffer layer, as depicted in Figure 1.8(b). Initially, this graded buffer layer contains no As content at the GaP nucleation layer interface, aligning with Si lattice constants, and gradually increases As content to accommodate the desired III-V-based layer [46].

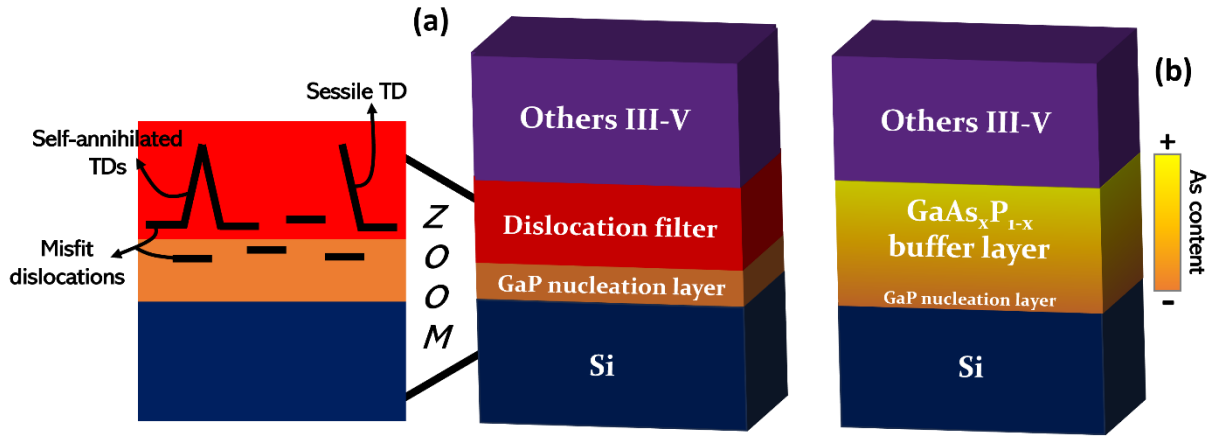


Figure 1.8. Schematic depiction of GaP-based layers on Si. Design (a) showcases a GaP nucleation layer on Si, serving as a platform for the deposition of other III-V materials, accompanied by a dislocation filter layer. The conceptual illustration on the left highlights the presence of misfit and potential threading dislocations within the dislocation filter. In design (b), the configuration remains consistent, albeit with a graded $\text{GaAs}_x\text{P}_{1-x}$ buffer layer. Layer thicknesses in the representations are not drawn to scale.

This design has proven effective in multijunction PV systems. Table I.II outlines typical values for solar cells utilizing this configuration. The attractiveness of this design stems from its dual role as a buffer layer: it serves to match the lattice constants of both the Si substrate and the upper III-V active layers, while also retaining TD within its thick structure. Despite GaP's high bandgap, rendering it non-absorptive for photons in the Si bottom cell, the gradual introduction of As into GaP lowers its bandgap, resulting in some parasitic light absorption. However, this compromise is preferable to the alternative of high TDD. To mitigate this bandgap reduction, aluminum can be incorporated into regions of the buffer layer with elevated arsenic content [47]. The solar cell parameters for this configuration are also presented in Table I.II under the designation of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$. To address cracking issues in

other devices, a strategy involves increasing the arsenic content towards the end of the graded buffer layer to match closely the TEC with the AlGaAsP/GaAs tunnel junction between the active layers and the graded buffers. Despite achieving favorable performances, this design exhibits a limitation in the efficiencies (around 22% as Table I.II indicates) of the final device. The presence of TD within the active layers leads to a loss of usable minority carriers in the output current, a phenomenon elaborated upon in detail in following sections (1.2.3.3). Another approach to address this issue involves the utilization of wafer bonding, briefly defined as the bonding of different layers grown separately, as applied in [48] and also indicated in Table I.II. It is important to note that the higher V_{oc} observed is attributed to two primary factors: the presence of GaInP as the active layer, which possesses a higher bandgap compared to GaAsP, and the absence of TD in the structure. However, despite its effectiveness in mitigating TD, wafer bonding is associated with high costs and complexity. Therefore, its mention here serves solely as an illustrative example of various methods employed to achieve such solar devices.

	TJSC			DJSC			
	GaInP GaAsP GaAs _x P _{1-x} GaP Si	GaInP GaAs GaAs _x P _{1-x} GaP Si	GaInP GaAs Al _y Ga _{1-y} As _x P _{1-x} GaP Si	GaAsP GaAs _x P _{1-x} GaP Si	GaAsP GaAs _x P _{1-x} GaP Si	GaAsP GaAs _x P _{1-x} GaP Si	GaInP GaAs GaP Si
Method	MOVPE	MOVPE	MOVPE	MOVPE	MOVPE	MBE	MOVPE
V_{oc} (V)	2.56	2.619	2.646	1.663	1.62	1.692	2.385
J_{sc} (mA/cm ²)	5.4	10	12.2	16.73	10.2	15.94	12.70
FF (%)	79	85	80.2	78.2	79.5	77	85.9
η_{Eff} (%)	-	22.3	25.9	21.8	13.3	19.99	26
ARC	No	Yes	Yes	Yes	No	Yes	Yes
TDD (cm ⁻²)	$5 \cdot 10^6 - 10^7$	$2.2 \cdot 10^7$	$1.5 \cdot 10^7$	$\sim 2 \cdot 10^7$	$\sim 2 \cdot 10^7$	$8 \cdot 10^6$	$\sim 0^*$
Reference	[49]	[50]	[47]	[51]	[51]	[52]	[48]

*Wafer bonding

Table I.II. Solar cell parameters for two types of multijunction solar cells. On the left side, parameters for triple junction solar cells are listed, while on the right side, parameters for double junction solar cells are provided. The respective structures are indicated in the heading cells for easy reference.

1.2.3.2 Ge deposition on Si

Incorporating Ge with Si offers an alternative avenue, particularly due to the good lattice matching between Ge and III-V material such as GaAs-based compounds and Ga_xIn_{1-x}P (with x around 0.5), as highlighted in the shaded area of the Figure 1.6. Serving as a bridge, Ge is used to try to accommodate the lattice parameters of both III-V materials and Si in an effort to alleviate the occurrence of threading dislocations within the material.

Certain challenges must be tackled in the integration of Si with Ge and III-V semiconductors. The lattice mismatch between III-V (or Ge) and Si can lead to defects and dislocations [53], which can impact the overall device performance [54]. Similarly to the observations made in the GaP/Si configuration, the differences in TEC pose significant challenges during the growth phase. Table I.III provides an overview of the TEC values for Ge, GaAs, Ga_{0.5}In_{0.5}P, and Si, revealing again that α_{TEC}^{Si} is approximately half as low as that of the other materials. This marked contrast adds considerable difficulty to high-temperature growth techniques such as MOVPE to obtain crack-free layers, as discussed in the preceding section.

	Si	Ge	GaAs	Ga _{0.5} In _{0.5} P
$\alpha_{TEC} (10^{-6} K^{-1})$	2.6	5.7	5.7	5.35

Table I.III. TEC values for a range of materials. The TEC values for Si, Ge and GaAs were obtained from [43], whereas the TEC value for Ga_{0.5}In_{0.5}P is cited from [55].

An already-used application lies in the strategic utilization of graded GeSi layers in conjunction with III-V materials on Si substrates. This configuration initiates with a Si layer smoothly transitioning into a germanium-silicon (GeSi) alloy until reaching the complete transition to Ge, accommodating the lattice mismatch between the Si substrate and subsequent III-V layers. Beyond serving as a scaffold for optimal epitaxial growth, the graded GeSi structure also contributes to defect and dislocation mitigation. Although this approach has achieved a relatively low TDD ranging between $5.4 \cdot 10^5 \text{ cm}^{-2}$ [56] and $2.1 \cdot 10^6 \text{ cm}^{-2}$ [57], achieving such low TDD values demands substantial GeSi layer thicknesses, up to tenths of μm , introducing material expenses and resulting in a rough surface morphology that may adversely affect the quality of deposited upper layers. For instance, in cases with a TDD of $2.1 \cdot 10^6 \text{ cm}^{-2}$ and a thickness of 12 μm , the resulting RMS of roughness ranged from 24 to 47 nm when the typical RMS roughness of standard Ge is lower than 1 nm [58].

A more straightforward approach involves the direct deposition of Ge on Si as an independent buffer layer. However, the absence of a graded GeSi buffer causes the persistence of lattice mismatch effects, with misfit dislocations originating from this mismatch [59]. Techniques for Ge deposition on Si include MBE [60], [61] and MOVPE, which has gained prominence in recent decades [62]. CVD has been extensively employed for this purpose. TDD in direct Ge deposition varies with Ge thickness and growth processes. Researches [63], [64] have shown that as Ge thickness increases, TDD decreases by two orders of magnitude, reaching its lowest levels when the thickness reaches 4 μm . Further reduction can be achieved through post-annealing, particularly with multiple cycles, resulting in a reduction of up to three orders of magnitude. Figure 1.9 illustrates the TDD values as a function of Ge thickness for the three

growth methods detailed in [64], including processes with and without post-annealing. Additionally, other techniques to enhance the dislocation movement by engineering the strain evolution using reverse grading have also shown promise [65].

Another strategy to mitigate threading dislocation appearance involves initially depositing a heavily arsenic-doped Ge seed layer on Si at low temperatures, followed by high-temperature deposition with a gradual reduction in arsine flow during growth to dope the layer with As [66]. This approach has been shown to reduce TDD by at least one order of magnitude compared to processes without arsenic doping, with TDD decreasing from $5.6 \cdot 10^7 \text{ cm}^{-2}$ to $4.6 \cdot 10^6 \text{ cm}^{-2}$. Additionally, the RMS roughness for samples with 1.5 μm of Ge thickness is among the lowest reported values at 0.37 nm. Figure 1.9 compares the TDD values under these two processes. More recent investigations have explored novel designs, such as patterning arrays of submicron-wide strips with rectangular cross-sections in the (110) direction of a Si wafer [67]. This study examined how TDD evolves as the spacing between patterned strips changes during Ge deposition of approximately 1 μm . The researchers found that narrower spacing between strips led to lower TDD values, suspecting that TD generation might be suppressed at the top surfaces of the strips due to induced structural degradation, leading to relaxation of compressive strain in Ge rather than TD generation. The most significant reduction in TDD was four times lower than the TDD observed in growth on planar Si, approximately $2 \cdot 10^8 \text{ cm}^{-2}$ under their CVD process. Figure 1.9 presents a summary of TDD values as a function of Ge thickness for the technologies mentioned above.

The utilization of Ge|Si virtual substrates fabricated by direct Ge deposition has found practical application in the field of PV. An investigation on a GaAs SJSC [68] exemplified the efficacy of heavily As-doped Ge buffer layers discussed earlier [66]. This SJSC capitalizes on the low TDD achievable with this type of Ge layer, achieving a V_{oc} of 900.2 mV and a J_{sc} of 19.56 mA/cm^2 under AM1.5G conditions. With an efficiency of 11.88%, this SJSC demonstrates potential for further improvement, potentially reaching 16% efficiency with the incorporation of an ARC. Subsequent research examined a similar design but utilized standard Ge without heavy doping [69]. This study assessed the impact of the estimated 10^8 cm^{-2} TDD in the initial Ge|Si virtual substrate on the GaAs active layer. A 1.5- μm GaAs buffer layer was employed to trap TDs before they could reach the active layer. Analysis revealed varying TDD values in the emitter and base regions. The emitter exhibited a TDD of 10^5 cm^{-2} in the 0.25- μm GaAs layer, while the GaAs base, with an estimated thickness of 2.5 μm , displayed a higher TDD of 10^7 cm^{-2} , significantly influencing device performance due to its wider thickness. Data from these GaAs SJSC experiments are presented in Table I.IV. Another SJSC employing this alternative

virtual substrate featured GaInP as the active cell [70]. Performance metrics for this solar design are also detailed in Table I.IV for comprehensive comparison.

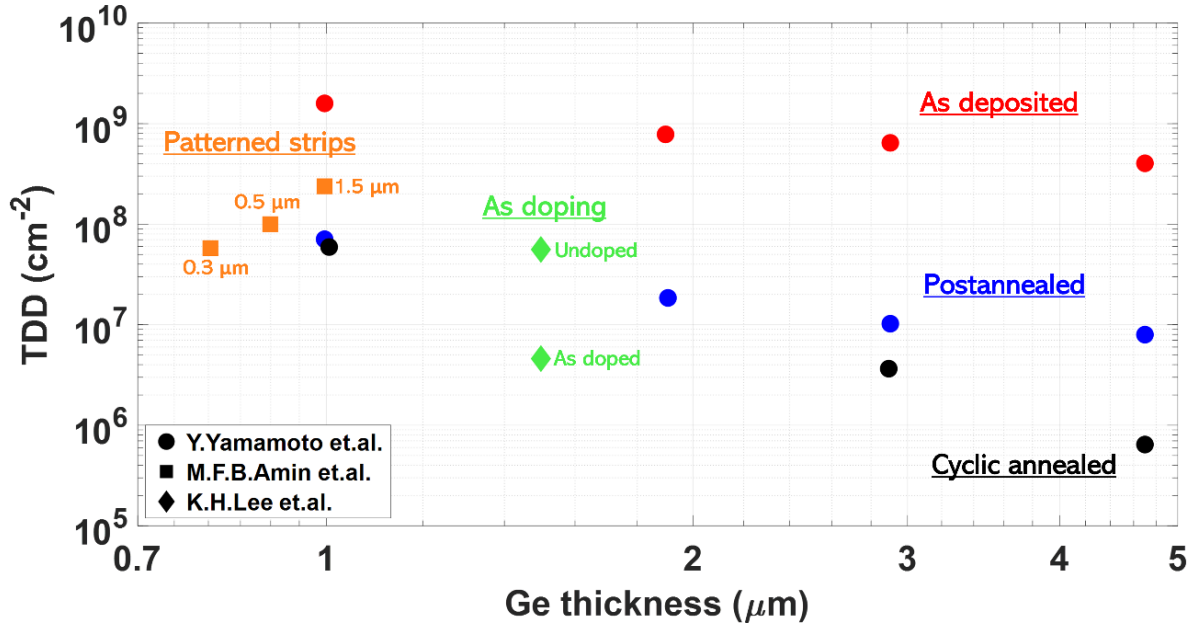


Figure 1.9. TDD values for three different methods of Ge deposition on Si as a function of Ge thickness. The filled circles represent data from [64], the orange squares denote values obtained from [67] and the green diamonds are extracted from [66]. The colored tags indicate the separation space among patterned strips (orange) and the TDD values when arsenic doping is not conducted for the same process (green).

In MJSC configurations utilizing Ge|Si substrates, investigations have been conducted on GaInP/GaInAs/Ge|Si DJSCs [71]. The approach involved wafer bonding, wherein the individual layers of SiO₂|Si and the GaInP/GaInAs/Ge structure were joined together. This bonding method circumvents the issue of TD propagation typically associated with III-V deposition on Ge|Si substrates, leading researchers to deem TDD insignificant. Operational devices resulting from this technique achieved a V_{oc} of 2.09 V and an efficiency of 15.5% without the use of an ARC.

On a different front, GaInP/GaInAs/Ge|Si TJSCs with Ge as bottom cell were deposited on a patterned Si substrate to address the lattice mismatch issue [72]. These alternative substrates were patterned with equally spaced pitches to accommodate the 4.2% lattice mismatch between Ge|Si and the upper III-V layers, thus impeding the formation of TD. However, the introduction of spaced patterned pitches led to the occurrence of step bunching due to changes in growth rates near the pitches, resulting in irregular deposition and the formation of dendritic or polycrystalline growth structures. Despite these challenges, operational devices were successfully fabricated, with the most favorable solar cell configuration featuring a pitch separation of 1.5 μm, yielding a V_{oc} of 2.47 V and an efficiency of 75.6%. This approach

demonstrates significant potential, especially considering that the same TJSC design on standard Ge substrates achieved a V_{oc} of 2.87 V and a FF of 85.5%. Table I.IV presents the parameters for these MJSCs on Ge|Si substrates. It is noteworthy that the TJSC experiment was conducted under 1000 suns illumination, which led to higher performance values compared to those obtained under standard 1-sun conditions.

Method	SJSC			DJSC	TJSC
	GaAs	GaAs	GaInP	GaInP	GaInP
	Ge:As	Ge	Ge	GaInAs	GaInAs
	Si	Si	Si	Si	Patterned Si
	MOVPE	MOVPE	MOVPE	MOVPE	MOVPE
V_{oc} (V)	0.9002	0.9	1.15	2.09	2.47 ± 0.04
J_{sc} (mA/cm ²)	19.56	23.29	10.8	9.5	$(1.04 \pm 0.01) \cdot 10^3$
FF (%)	67.47	74	61.7	79	75.6 ± 3.2
η_{Eff} (%)	11.88	11.48	22.1	15.5	19.3 ± 1.2
Spectrum	AM1.5G	AM0	AM1.5D*	AM1.5D	AM1.5D***
ARC	No	-	No	Yes	No
TDD (cm ⁻²)	$< 5 \cdot 10^6$	$\sim 10^7$	$1.5 \cdot 10^7$	$\sim 0^{**}$	$\sim 10^7$
Reference	[68]	[69]	[70]	[71]	[72]

*Spectrum between 517 nm and 652 nm

**Wafer bonding

*** x1000 suns

Table I.IV. Solar cell parameters for various configurations utilizing Ge|Si virtual substrates. Parameters for single-junction solar cells are listed on the left side, while those for double-junction solar cells are provided in the middle. Additionally, parameters for triple-junction solar cells are indicated on the right side. The corresponding structures are specified in the heading cells for convenient reference.

The importance of buffer layer thickness has been reiterated throughout the discussion, given its impact on the TDD obtained and on the usage of Ge. Using ultra-thin Ge layers have been proposed [73]. However, challenges akin to those encountered with GaP and thicker Ge buffer layers persist in this configuration. The critical consideration here is the ultra-thin nature of the Ge buffer layers, even measuring tenths of nm and not exceeding a micron in thickness. This thinness poses a challenge, as the narrow width is insufficient for potential TD to self-annihilate [74], as observed in thicker layers. Consequently, existing dislocations are more likely to propagate into upper layers, impacting negatively the efficiency of semiconductor devices. In response to this challenge RF-PECVD has emerged as a promising technique. In RF-PECVD, a low-pressure plasma environment is created in a vacuum chamber by applying radio

frequency energy to a gas mixture containing precursor gases. The plasma consists of a highly energetic and ionized gas, which interacts with the precursor gases to produce reactive species such as ions, radicals, and excited molecules. These reactive species chemically react with the substrate surface, leading to the deposition of thin films with controlled composition, thickness, and properties. The RF energy applied to the plasma also plays a crucial role in enhancing the chemical reactions and promoting the decomposition of precursor molecules. Furthermore, the use of RF energy allows for the generation of a stable and uniform plasma discharge, ensuring uniform deposition across large substrate areas. RF-PECVD offers advantages such as high deposition rates, precise control over film properties and low substrate temperatures. The use of low temperatures minimizes post-processing variations, especially in cases where extended cooling periods are necessary. This characteristic is advantageous as it helps prevent significant differences in TEC among the materials involved. This technique has demonstrated success in achieving a TDD of approximately 10^6 cm^{-2} with a thickness of 170 nm [75]. This method holds promise, particularly due to its closer proximity, with a reduced thickness, to the TDD observed in thicker Ge layers discussed previously. It can be advanced that an important focus of this Thesis revolves around an in-depth examination and understanding of these ultra-thin Ge|Si virtual substrates, aiming to assess their applicability to photovoltaic applications.

1.2.3.3 Effects of threading dislocations on device performance

Before continuing with the applications of Ge|Si virtual substrates in PV, it is important to briefly expound upon the negative impact of TDs. When electrons are promoted to the conduction band, creating holes in the valence band (Figure 1.4), they eventually reoccupy the valence band, annihilating the created holes. This phenomenon prevents the participation of these electrons in the output current, thereby compromising the overall efficiency of the solar device. The carrier lifetime (duration of an electron to return to the valence band) is contingent on various factors, with the semiconductor's quality being a critical determinant. Notably, the presence of defects, such as the aforementioned TDs, significantly influences the carrier lifetime. To succinctly show the impact of TDs on the effective minority carrier lifetime (τ), the following expressions are employed [53], [76]:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_{TDD}} \quad (\text{Eq. 1.3})$$

$$\frac{1}{\tau_{TDD}} = \frac{\pi^3 D_{n,p} N_{TDD}}{4} \quad (\text{Eq. 1.4})$$

In order to relate the direct impact of TDD and its consequential carrier lifetimes on solar device performance, it is essential to establish correlations with the operational

characteristics of the solar device. To accomplish this, we turn to the ideal diode equation (neglecting series or shunt resistances and assuming an ideal factor of 1). The current density is defined by the equation:

$$J = J_L - J_{Diode} = J_L - J_0 \left[e^{qV/k_B T} - 1 \right] \quad (Eq. 1.5)$$

Here, J_L is the photogenerated current density. Meanwhile, J_0 represents the saturation current density of the equivalent diode. The intrinsic impact of TDD is encapsulated within the definition of J_0 which reflects carrier lifetimes [77]:

$$J_0 = qn_i^2 \left(\frac{1}{N_D} \sqrt{\frac{D_p}{\tau_p}} + \frac{1}{N_A} \sqrt{\frac{D_n}{\tau_n}} \right) \quad (Eq. 1.6)$$

Consider a scenario with a front junction and a rear heterojunction, where the emitter thickness is significantly thinner than that of the base in the former case, and vice versa in the latter. Hence, regarding the wider region of the solar device as dominant is a suitable approximation. As a solar cell necessitates the existence of pn or np junctions, these dominant regions can behave solely as n or p, thereby simplifying J_0 :

$$J_0^n \cong q \frac{n_i^2}{N_D} \sqrt{\frac{D_p}{\tau_p}} \quad (Eq. 1.7)$$

for the n-type case, and

$$J_0^p \cong q \frac{n_i^2}{N_A} \sqrt{\frac{D_n}{\tau_n}} \quad (Eq. 1.8)$$

for the p-type case.

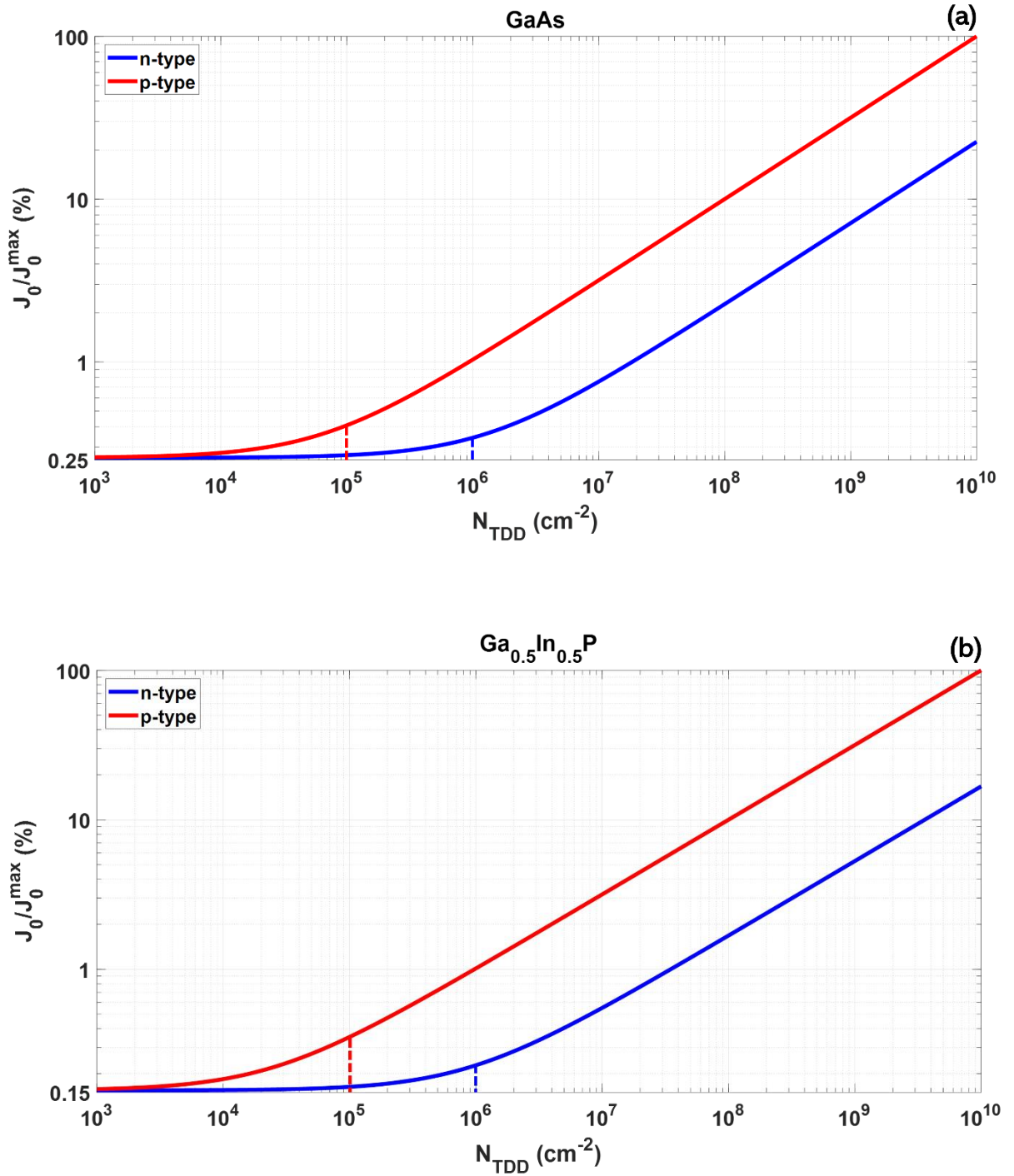


Figure 1.10. Plots illustrating $J_0/J_0^{\max}$ as a function of TDD values for GaAs (a) and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ (b), doped as both n-type and p-type semiconductors with a concentration of 10^{17} cm^{-3} for all cases. Dashed lines indicate the value of TDD where the ratio experiences a considerable and constant increase.

For a more practical perspective, the application of these equations is qualitatively analyzed for semiconductors such as GaAs and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$. The way to proceed is the following. The procedure involves the calculation of minority carrier diffusion coefficients using Einstein's relation:

$$D_{n,p} = \frac{k_B T}{q} \mu_{n,p} \quad (\text{Eq. 1.9})$$

where T is set to 300 K and the minority carrier mobility μ (at 300 K) is obtained numerically in [78]. Subsequently, the calculation of τ_0 is derived from the radiative lifetime formula:

$$\tau_0 = \frac{1}{B \cdot N_{\text{Dopant}}} \quad (\text{Eq. 1.10})$$

The utilized values of B (at 300 K) are $B_{\text{GaAs}} = 7.2 \cdot 10^{-10} \text{ cm}^3/\text{s}$ [79] and $B_{\text{Ga}_{0.5}\text{In}_{0.5}\text{P}} = 1.6 \cdot 10^{-10} \text{ cm}^3/\text{s}$ [80].

Figure 1.10 illustrates the evolution of the ratio J_0/J_0^{max} , where J_0^{max} corresponds to the most unfavorable case within the analyzed range with $N_{\text{Dopant}} = 10^{17} \text{ cm}^{-3}$. The chosen values were applied separately for GaAs and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, while J_0^{max} corresponding to the p-type version of each material with $N_{\text{TDD}} = 10^{10} \text{ cm}^{-2}$. A brief examination of Eq. 1.5 and Eq. 1.6 reveals that a smaller J_0 is advantageous to maximize J . Thus, a high lifetime is desirable and achievable with low TDD, which tends to make τ_{TDD} approach infinity, as illustrated in Eq. 1.3 and Eq. 1.4.

In considering the normalization against the most adverse J_0 , it becomes apparent that both GaAs and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ are equally susceptible to the effects of TDD. Although GaAs shows a 0.10% higher loss at the lowest TDD, this difference is negligible considering the ratio is expressed in percentage terms. An interesting observation emerges when comparing losses between different dopant types. Specifically, n-type semiconductors endure the least losses. This can be straightforwardly explained: as indicated by Eq. 1.3 and Eq. 1.4, when electrons serve as minority carriers in p-type semiconductors (typically exhibiting faster diffusion compared to holes in n-type), τ_{TDD} tends to decrease, resulting in a reduction in available output current. In practical terms, this suggests that the likelihood of interactions between TD and minority carriers increases with the velocity or diffusion of these minority carriers. This trend is manifest in the TDD values where the J_0 begins to escalate rapidly and unfavorably. For n-type cases, it remains around 10^6 cm^{-2} (blue dashed lines), while for p-type cases, it is approximately 10^5 cm^{-2} (red dashed lines). Achieving these low TDD values is challenging, as previously discussed concerning GaP/Si and Ge/Si substrates, emphasizing the significance of technological advancements aimed at their reduction, particularly given the cost-effectiveness associated with the use of Si.

TDs can also detrimentally impact the collection capacity of an active subcell, consequently diminishing its IQE. This decline in IQE is intricately linked to a lower minority carrier diffusion length [81] and, consequently, the minority carrier lifetime. As a result, the deterioration in

IQE due to poorer lifetimes exerts a negative influence on both J_{sc} and V_{oc} , leading to a decrease in their respective values. Moreover, the presence of TD may contribute to a reduction in shunt resistance [82], thereby further diminishing the FF. Whether TD impacts J_{sc} , V_{oc} and FF individually or collectively, the outcome remains consistent: a decrease in overall efficiency, given the direct proportionality of these parameters to efficiency.

1.2.4 Multijunction solar cells on Ge-based substrates at IES-UPM

The *IES-UPM* has been actively engaged in PV research, particularly within the III-V semiconductor group, with a focus on enhancing the efficiency of multijunction solar cells. Despite the ample multijunction configurations under research at IES-UPM, the GaInP/GaInAs/Ge TJSC stands out as a remarkable technological achievement, boasting efficiencies above 40% under concentrated light [83] after building upon the success of achieving record-breaking performance with dual-junction solar cells under high concentration [84]. In a continued quest for higher efficiencies, the IMM design, with a subcell bandgap combination with higher potential, was also developed [85]. Furthermore, recent advancements have showcased the considerable impact of improved ARC on this TJSC, resulting in efficiency gains of up to 1.8% [86].

In epitaxial considerations during the deposition of GaInP/GaInAs/Ge structures, special attention to various parameters is essential. Notably, the conditions governing nucleation deposition have proven crucial in influencing the ultimate performance of the devices, underscoring the necessity of precise control over this initial stage of deposition on Ge substrates [87]. Moreover, the management of surface roughness assumes great importance in minimizing the presence of undesirable recombination centers. To address this challenge, real-time analysis and monitoring tools, such as RAS in situ, have provided valuable insights into different nucleation routines and reactor conditions, offering valuable insights into their impact on the morphology of the grown layers [88]. As elucidated later, the phenomenon of Ge outdiffusion presents a significant obstacle during deposition on Ge substrates. To mitigate this issue, the incorporation of a low-temperature GaAs layer serves as an effective barrier, effectively curtailing unwanted doping in the upper active layers [89].

However, as the maturity of the MJSC technology was reaching high levels, the issue of production cost gained importance. As commented before, the high cost of III-V technology is determined mainly by the cost of the substrate and epitaxial deposition [90]. In addition, the scarcity of Ge as raw material imperils the deployment of the high efficiency III-V technology at high scale. Besides cost considerations, the life-cycle assessments of the high efficiency multijunction solar cell technology demonstrates a CED about one order of magnitude higher for Ge or GaAs substrates than for Si substrates [91].

Hence, one of the workhorses in the quest for lower costs of the III-V technology has been the replacement of expensive and scarce Ge substrates by “virtual” substrates based on Si. In the context of projects funded by the *Agencia Estatal de Investigación* (projects VIGNEMALE and ARISE), IES-UPM tackled this research line. Figure 1.11 shows a visual representation of the two virtual substrate target designs investigated at IES-UPM. Design I integrates a sufficiently thick Ge layer, while design II entails the deposition of a thin Ge film (a few nm) on Si. Moreover, the Germanium-On-Nothing approach (GON), not based on Si, is also under research. Subsequent sections will delve into these configurations, describing the results achieved before the work of this Thesis started.

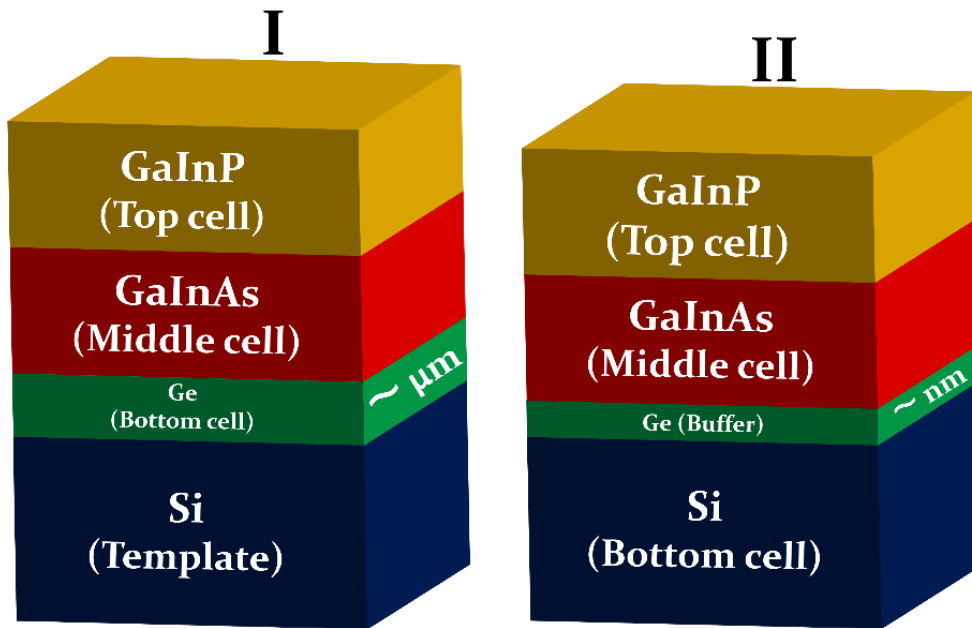


Figure 1.11. Schematic depiction of two Ge/Si virtual substrate designs. Design I illustrates a TJSC configuration with a sufficiently thick Ge layer (a few microns) serving as the active bottom cell. In Design II, the TJSC configuration is maintained, but the Ge layer is intentionally thin (a few nanometers), functioning solely as a bridge between GaInAs and Si.

1.2.4.1 Ge/Si virtual substrates with thick Ge layer functioning as bottom cell

The first virtual substrate design studied during VIGNEMALE project is based on a thick Ge layer deposited directly on Si. At the time this project started, the company IQE (UK) was developing this kind of virtual substrates, for all kinds of optoelectronic device applications, achieving very low TDD, below $1 \cdot 10^6 \text{ cm}^{-2}$ in their most advanced versions. In the context of PV, the work at IES-UPM focused on testing these virtual substrates for the epitaxial growth and fabrication of high efficiency III-V multijunction solar cells and tailoring the semiconductor structure to make it compatible with the virtual substrates.

In Figure 1.11, design I features Ge|Si substrates supplied by *IQE Corporation*, with a Ge layer of adequate thickness serving as the bottom cell. Thorough simulations indicated that a Ge layer thickness of 1-3 μm is adequate for maintaining the current matching characteristic of GaInP/GaInAs/Ge TJSC (14.5 mA/cm^2) [92], [93]. This estimation takes into account the recombination at the Ge|Si interface and the efficiency degradation associated with it. However, the first MJSC, aiming to achieve a proof of concept prototype, were implemented using virtual substrates with a 5- μm Ge layer [74], and a high TDD. The EQE measurements unveiled that the GaInAs middle cell exhibited a significantly lower EQE compared to TJSC on standard Ge substrate, whereas the GaInP top cell demonstrates virtually identical EQE in both scenarios. Analyzing the I-V curves, the Ge|Si samples exhibited a significant performance decline, aligning with the poor EQE. In terms of the open-circuit voltage a significant loss of approximately 0.5 V is observed compared to the standard Ge substrate. The observed poorer results can be attributed to two prevailing factors. Firstly, the existing TDD in the Ge|Si substrate, which stands at approximately $4 \cdot 10^6 \text{ cm}^{-2}$. As estimated using Figure 1.10, this value impacts the np GaInAs middle cell, resulting in a roughly 5% losses in J_0 if a substantial portion of these TDs extends to it. Secondly, the formation of new internal cracks in the GaInAs subcell. The emergence of these mechanical defects could be attributed to the temperature ramps employed during the growth of the second tunnel junction immediately after depositing the thick ($\sim 4 \text{ }\mu\text{m}$) GaInAs middle cell. Additionally, the presence of cracks in the structure can be accentuated by the different TEC of the layers involved. This supposition is substantiated by the visual evidence of cracks on the device surface through an optical microscopy image (Figure 1.12).

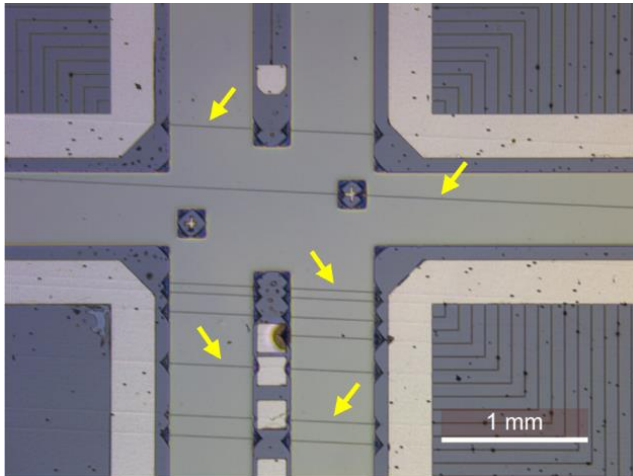
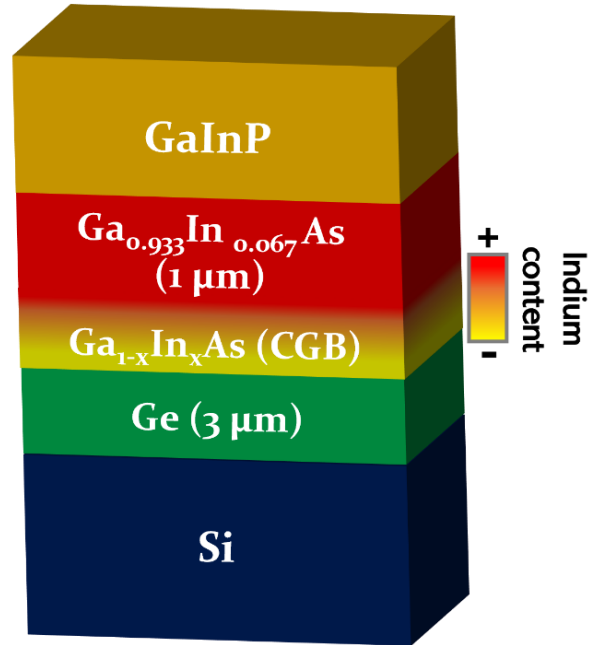


Figure 1.12. Frontal perspective of the TJSC with visible cracks traversing the device's surface. Highlighted by yellow arrows are instances of these cracks for reference.

These results demonstrated the concept but clearly showed room for improvement. While the effect of the TDD could be removed by using higher quality virtual substrates from IQE, the formation of cracks was deemed a more challenging issue. Virtual substrates with thinner Ge layers down to 3 nm, made available by IQE, could alleviate the problem. However, the

thickness of the TJSC III-V structure is already over 4 μm so the combined thickness of Ge + III-V surpassed the estimated critical thickness for the formation of cracks, around 5 μm . Therefore, an imperative next step involved minimizing the thickness of the III-V layer to avoid surpassing the critical thickness for crack formation [94]. Opting for a Ge thickness of 3 μm , efforts to further decrease the total thickness contemplated thinning the GaInAs middle cell, initially around 4 μm . However, the reduced light absorption in a thinned GaInAs subcell prompted using a lower bandgap, necessitating an additional indium (In) content. Simulation outcomes for a GaInP/GaInAs/Ge TJSC indicated an 8% In content requirement to sustain current matching with a GaInAs thickness of 1 μm . A CGB was designed and implemented to transition the composition (and lattice constant) of the GaInAs to achieve this In content, as depicted in Figure 1.13. The thickness of this CGB was kept as low as possible so as not to defeat the original purpose of thinning the whole III-V structure.

Figure 1.13. Structure of a metamorphic GaInP/Ga_{0.933}In_{0.067}As/Ge/Si, featuring a CGB to facilitate the accommodation of lattice constants between Ge and Ga_{0.933}In_{0.067}As.



In Figure 1.14(a), the EQE profiles of the top and middle cells within the TJSC are presented, offering a comparative analysis with a standard design on conventional Ge substrates. The Ge bottom cell is omitted from the display due to measurement challenges arising from its leaky behavior [95]. The GaInP top cell exhibits the anticipated absorption edge shift in both the absorber material and window layer, attributed to the extra In content. Similarly, the GaInAs middle cell displays a corresponding shift, accompanied by a reduced EQE compared to its standard Ge-based counterpart. This diminution in performance is attributed to lower material quality characterized by a TDD of $2 \cdot 10^7 \text{ cm}^{-2}$ and non-optimized CGB. However, these

functional cells proved to proof the concept as the density of cracks obtained decreased drastically, as shown in the inset of Figure 1.14(b).

Figure 1.14(b) illustrates the evolution of J-V curves for TJSCs as the III-V structure was thinned, accompanied by the progression of changes in In content. Firstly, a significant improvement in the J_{sc} was attained, as the quality of the GaInAs middle cell was improved. This J_{sc} can be further improved to match the TJSC on standard Ge substrate by using virtual substrates with lower TDD and redesigning the CGB and GaInP top cell for current matching. Second, the observed drop in V_{oc} can be attributed to two different factors. Firstly, there is a decrease of approximately 185 mV stemming from the lower bandgap in both the GaInAs and GaInP subcells due to the additional In content. Secondly, an additional V_{oc} reduction of approximately 78 mV is associated with the lower quality of the GaInAs subcell, as previously outlined.

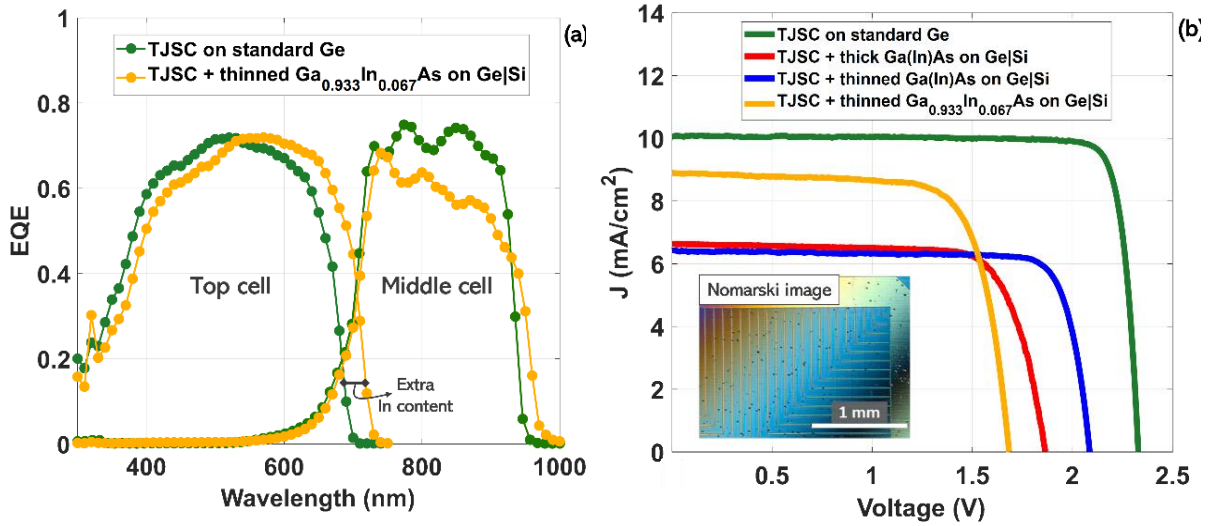


Figure 1.14. (a) EQE of the top and middle cells in the TJSC under examination. The dots represent experimental results for the TJSC on standard Ge substrates (yellow orange) and the TJSC with a thinned $Ga_{0.933}In_{0.067}As$ middle cell on a Ge|Si virtual substrate (green). (b) Representative J-V measurements of the TJSC developed on Ge|Si with varied thinning and In content, in comparison to the conventional design on a standard Ge substrate. Inset: Nomarski microscope image of the TJSC with thinned GaInAs on Ge|Si after growth.

Although there is a large room for improvement, these results demonstrated the viability of this kind of Ge|Si substrates for the implementation of III-V TJSC, and the path to achieve high performances. The $\sim 2\text{-}3\%$ lower efficiencies attainable in the thinned design could be affordable if the production cost of the Ge|Si virtual substrates are sufficiently reduced, as compared to standard Ge substrates.

1.2.4.2 Ultra-thin Ge|Si

A more aggressive option, in terms of Ge material usage and potentially lower cost, involves depositing a thin film (a few nm) of Ge on Si with the sole purpose of serving as a bridge between III-V materials and Si. In this configuration, named ultra-thin Ge|Si virtual substrates, Ge is intentionally maintained at a thickness insufficient for any useful light absorption to function as a subcell. In this case, the Si substrate functions as the bottom cell. The Ge|Si virtual substrates utilized in this study were provided by LPICM-CNRS of *Ecole Polytechnique* in Palaiseau, France, and the deposition process was carried out using the RF-PECVD method in a standard 13.56 MHz capacitively coupled RF-PECVD system, with detailed process parameters outlined elsewhere [75]. In pursuit of a high-efficiency GaInP/GaInAs/Ge|Si TJSC, illustrated in design II of Figure 1.11, a preliminary investigation is crucial to establish a functioning proof-of-concept [96]. Given the considerable lattice mismatch and the thin Ge thickness in the provided samples (ranging from 20 to 140 nm), a notable TDD in the Ge layer is expected, as elucidated in preceding sections. However, as reported in [75], TDD levels as low as 10^6 cm^{-2} have been attained, attributed to the benefits of employing low-temperature epitaxy. This approach eliminates thermal strain resulting from disparities in TECs.

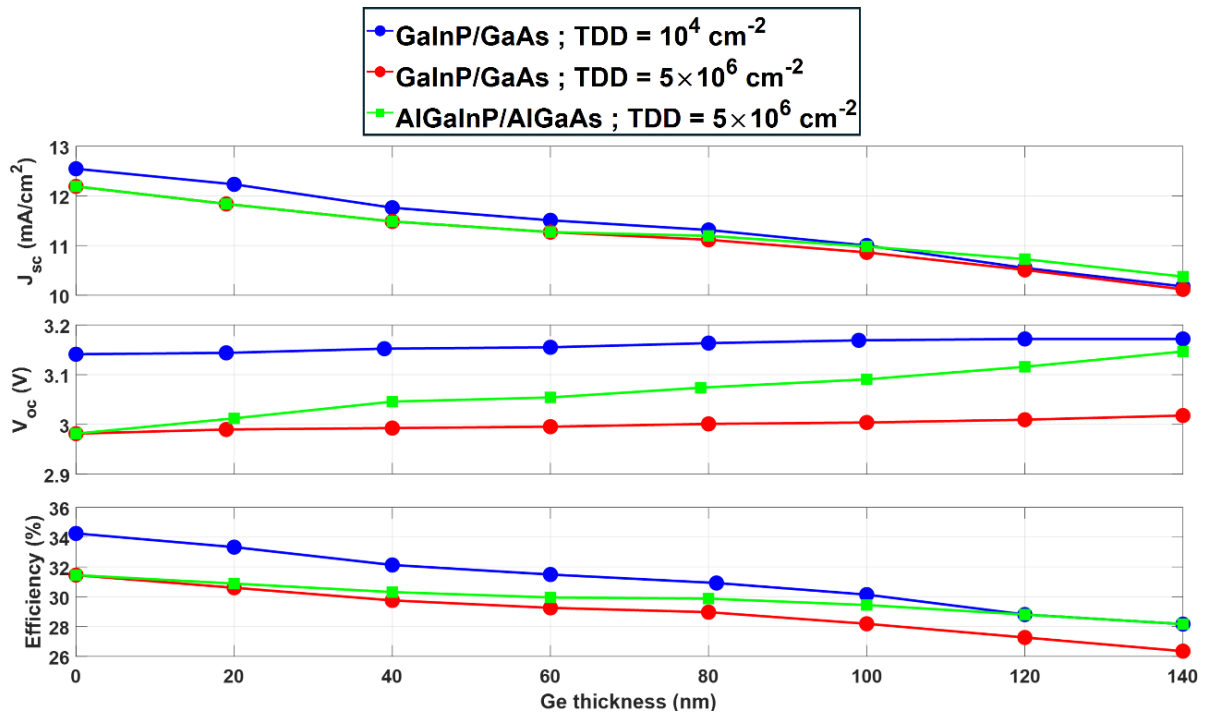


Figure 1.15. Simulated values for J_{sc} , V_{oc} , and efficiency at 1-sun for the optimized triple-junction solar cell on Ge|Si versus the thickness of the Ge layer, considering three different design scenarios.

The first work performed aimed to study the potential of these substrates for the implementation of high efficiency multijunction cells. Two main concerns were taken into account: the presence of dislocations and the parasitic light absorption in the Ge layer. Two

TDD scenarios were considered in TJSC simulations: negligible TDD (10^4 cm^{-2}) and the optimal value ($5 \cdot 10^6 \text{ cm}^{-2}$) obtained from the fabricated Ge|Si virtual substrates [75]. With the TDD range defined, two strategies were explored to achieve current matching across various Ge thicknesses: reducing the thickness of III-V active layers or increasing the bandgap of these layers through aluminum incorporation. The impact of Ge thickness on J_{sc} , V_{oc} and η_{Eff} was elucidated (see Figure 1.15). As the Ge layer increases, so does the Si bottom cell photocurrent loss and the upper subcells must be thinned or their bandgap increased, to achieve current matching. Obviously, the J_{sc} decreases but the V_{oc} benefits from thinner and/or higher bandgap absorber layers in the upper subcells. The main conclusion was that the impact on the overall efficiency is expected to be unacceptable for the highest Ge thickness considered. For thicknesses around 40 nm the efficiency loss is 2% absolute, which could be acceptable in a scenario of much lower substrate cost and Ge usage.

Concerning experimental studies, firstly thin Ge layers with a thickness of 20 nm were utilized as virtual substrates for the fabrication of prototype GaInAs/Ge|Si DJSC, as illustrated in the inset of Figure 1.16(b). The EQE and J-V curves, presented in Figure 1.16, demonstrate the functionality of the devices and indicate reasonable performance for an initial attempt with ultrathin Ge|Si virtual substrates. In Figure 1.16(a), an analysis of the EQE data suggests a Si bottom cell with moderate back surface recombination (approximately 10^4 cm/s) and a base lifetime exceeding $1 \mu\text{s}$, as expected for the fabrication conditions used. The GaInAs subcell exhibits EQE limitations due to the low diffusion length in the base, below 600 nm, caused by too high TDD in the virtual substrates used.

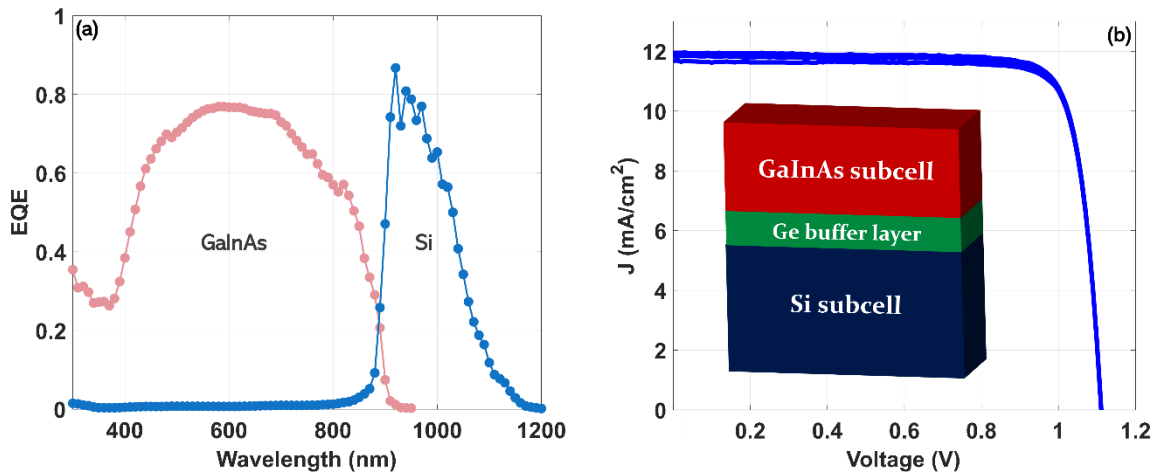


Figure 1.16. (a) Experimental EQEs of GaInAs/Ge|Si. (b) Light J-V curves of the same DJSC configuration. Inset: Schematic representation of the GaInAs/Ge|Si DBJS.

The light J-V curves (Figure 1.16(b)) reveal a V_{oc} of around 1.1 V with potential for improvement, considering that high-quality GaInAs/Si devices can achieve a V_{oc} of 1.4 eV [97]. The presence of a high TDD likely contributes to the observed V_{oc} loss.

In view of these experimental results, which indicate a much higher TDD than reported in the literature [75], the work planned for this Thesis was to ascertain the quality of the virtual substrates and the potential to improve it, in collaboration with LPCIM-CNRS.

1.2.4.3 Germanium-On-Nothing

Another virtual substrate based on Ge but without incorporating a Si substrate had been started to be tested in a collaboration between *UMICORE*, *IMEC* (Belgium) and IES-UPM. In this virtual substrate concept the epitaxy of Ge on a substrate with dissimilar lattice constant is not used, aiming to eliminate the limitation posed by the formation of dislocations and cracks. The concept, known as GON, is based on creating a releasable Ge film on the surface of a standard Ge substrate. This template can be used to fabricate releasable multijunction solar cell structures. The Ge substrate can then be reused multiple times.

Figure 1.17 provides a detailed illustration of the manufacturing process for such substrates. Initially, a Ge bulk substrate undergoes a series of lithography and dry etching steps to create a weakened layer beneath the foil. This process of Ge-on-Ge engineering begins with the patterning of deep micropitches, followed by a subsequent annealing step where the micropitches coalesce, ultimately restructuring the front surface into the mentioned foil, thereby forming the GON structure. Once this foil is obtained, the next step involves epitaxial growth of III-V materials on it to achieve the desired configuration based on the intended purpose. Leveraging the rigidity of the columns that support the upper foil prior to detachment, various device processing tasks, such as metallization or lithography and etching on the newly deposited III-V material, can be performed. Upon completion of the entire process, the foil should be readily detachable from the mother substrate, leaving behind a pristine Ge surface for further epitaxial growth until the material is fully depleted. Subsequently, the detached substrates must undergo epitaxial reconditioning for future depositions. The application of this process with Ge draws confidence from its successful implementation with porous Si, as demonstrated in prior studies [98].

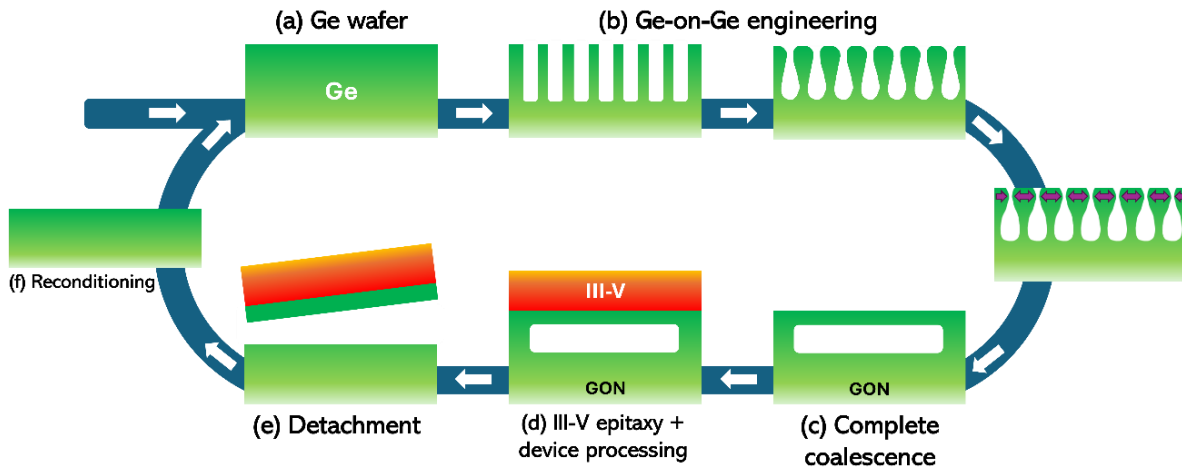


Figure 1.17. Schematic representation of the iterative fabrication process for Ge-on-Ge engineering: (a) A Ge wafer undergoes (b) lithography and dry etching steps to create micropitches, initiating the formation of a Ge-on-Ge structure. Subsequent annealing facilitates the coalescence of micropitches until (c) complete merging occurs, resulting in a suspended foil. (d) III-V semiconductors are epitaxially deposited onto the foil to establish the future solar device after undergoing prior processing. Finally, (e) the heterojunction is detached, and the remaining Ge is reused after (f) reconditioning, returning to step (a). This iterative process continues until the Ge wafer is depleted.

Ge, aside from being a valuable and indispensable raw material [99], plays a pivotal role in the composition of III-V multijunction solar cells, significantly contributing to their overall weight. With the aim of enhancing the specific power (W/kg) of these solar cells, efforts are directed towards reducing the thickness of the germanium substrate. To assess its feasibility, a GON substrate with a foil thickness of $1.3\ \mu\text{m}$ underwent a MOVPE process, during which a GaInP nucleation layer and GaInAs overbuffer layer were deposited [100]. This initial approach withstood the epitaxial growth process, considering factors such as thermal load and the additional weight of III-V layers. Furthermore, the light heterojunction was successfully detached using the Lift-off method, as demonstrated in Figure 1.18.

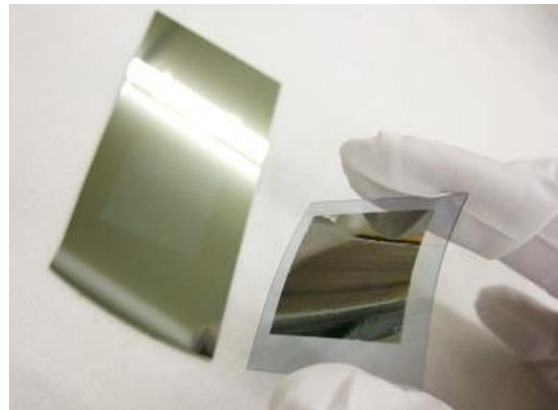


Figure 1.18. The Lift-off of a Ge foil from a Ge-on-Ge engineered substrate, with the foil measuring $1.3\ \mu\text{m}$ in thickness.

Following the successful demonstration of its reliability, research was conducted on a SJSC based on GaInP/GON [101]. Despite some issues that need to be addressed, such as reducing surface roughness post-deposition, the substrates exhibited minimal residual strain compared to bulk Ge substrates. Figure 1.19 illustrates the EQE measurements for the GaInP junction. Cells grown on standard bulk Ge and Ge-on-Ge engineered areas showed virtually identical EQE profiles. Light I-V curves were measured under 1 sun AM1.5D conditions, resulting in a V_{oc} of approximately 1.215 V. Considering that the V_{oc} on standard bulk Ge typically hovers around 1.225 V, this outcome holds promise. Further support for these substrates can be found in Table I.IV. Focusing on the V_{oc} for the same GaInP SJSC on Ge|Si substrates reveals an improvement of approximately 0.1 V, likely attributable to the absence of TD in the latter design.

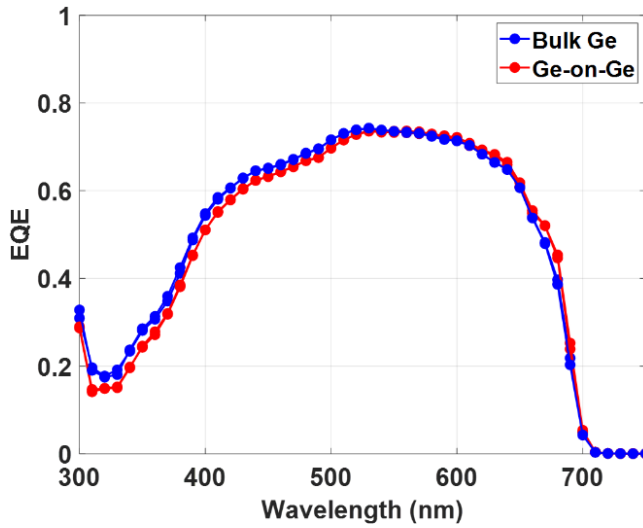


Figure 1.19. EQE measurements obtained from devices fabricated on bulk Ge substrate (blue) are compared with those from devices fabricated on Ge-on-Ge engineered substrate (red).

During this Thesis, the technology of GON was further tested on full triple-junction solar cells, as detailed in Chapter 5.

1.3 Objective and Thesis organization

This Thesis takes the lead from previous studies at IES-UPM, summarized in last sections, to continue investigating the suitability of virtual substrates based on Ge|Si for the implementation of high efficiency III-V multijunction solar cells. Hence, the global objective is to expand the knowledge base necessary to appraise the suitability of these virtual substrates and, ultimately, select the most appropriate technology for the implementation of state-of-the-art multijunction cells.

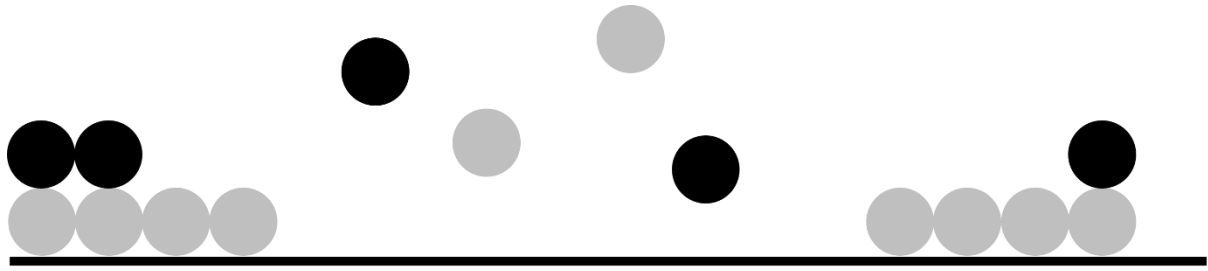
In this context, the Thesis is structured into two main blocks, each addressing different facets of the research conducted. Prior to delving into the primary researches, Chapter 2 provides

an overview of the methodologies employed for sample preparation and measurement. Block I, which focuses on Ge-based substrates, is divided into two chapters: Chapter 3 presents a detailed analysis of the measurements obtained, with particular emphasis on Ge|Si virtual substrates. Chapter 4 explores our preliminary studies of GON substrates within the framework of photovoltaic applications. Block II consists of a single chapter (Chapter 5) dedicated to investigating the diffusion of arsenic into germanium during a MOVPE process. Finally, Chapter 6 outlines potential future research directions and experimental strategies to further advance the work presented in this Thesis.

In advanced and in a bit more detail, these Thesis chapters will consist of:

- **Chapter 2** presents a comprehensive overview of the methodology, describing the sequential steps involved in the MOVPE growth and subsequent sample measurements. The characterization of Ge-based substrates is crucial for optimizing growth processes and understanding their implications on device functionality. Various techniques, such as AFM and TEM, were employed for morphological measurements. To analyze the dopant profile within the samples, ECV and SIMS techniques were utilized to assess active and chemical doping profiles. Additionally, the quality of the epitaxially deposited layers was evaluated using EBSD and ECCI. It is important to note that these methods represent a subset of the comprehensive characterization toolbox employed, and the chapter provides illustrative examples of the methodologies used for a thorough understanding of the epitaxial structures.
- **Chapter 3 of block I** provides an extensive analysis focusing on ultra-thin Ge|Si virtual substrates and their subsequent GaAs deposition. The investigation meticulously examines the morphological and structural characteristics of these samples, aiming to identify and characterize defects such as TDs. These defects often arise due to the inherent lattice mismatch between Si and Ge, both within the Ge|Si virtual substrates and as they propagate into the deposited GaAs layer. Furthermore, the study includes an exploration of plastic deformation across the sample surfaces, offering insights into the distribution and extent of strain induced during epitaxial growth. Finally, the chapter briefly discusses the diffusion of elements from the GaAs layer into the virtual substrate.

- **Chapter 4 of block I** delves into the outcomes derived from GON substrates, a novel Ge-based substrate that underwent a proof-of-concept evaluation by epitaxially depositing GaInP/GaInAs/GON triple-junction solar cells. The reliability of these solar cells was evaluated using standard procedures for solar cell characterization following III-V epitaxial deposition and subsequent processing to achieve functionality as a solar device.
- The research in **Chapter 5 of block II** focuses on As diffusion into Ge during MOVPE, aiming to unravel thermodynamic influences on dopant profiles. The development of diffusion simulations, their comparison with experimental results, and theorization of causes behind profile changes during various MOVPE stages are explored. It's noteworthy that the research utilized standard Ge wafers due to their thickness of the ultra-thin Ge|Si virtual substrates, allowing for easier diffusion and subsequent analysis.
- In **Chapter 6**, the thesis concludes with a summary and synthesis of the discussions and findings from the previous chapters, providing a concise overview to understand the key concepts and main insights of the entire work. The chapter then concludes with a discussion on potential directions for future research, building upon the findings presented in this study. This section offers a roadmap for prospective investigations, highlighting areas that merit further exploration and expansion.



Methodology

CHAPTER 2

This chapter serves as a guide to explain the procedures involved in both the deposition and subsequent measurements performed on the samples under scrutiny. The aim is to provide readers with a systematic understanding of the entire process. Each section catalogues the specific techniques employed at various stages of sample analysis. Furthermore, the chapter succinctly outlines the characterization methods utilized throughout, facilitating the interpretation and analysis of the measurement outcomes.

2.1 Epitaxial deposition by MOVPE

2.1.1 MOVPE fundamentals

The MOVPE technique stands as a cornerstone in the fabrication of III-V semiconductor-based solar cells, representing the predominant method in both research and industrial settings. Renowned for its versatility and scalability, MOVPE facilitates the growth of semiconductor structures boasting precise composition, doping profiles, and thicknesses spanning from the nanoscale to the microscale, all optimized for large-scale production. In this section, the fundamental principles underlying the MOVPE method is briefly introduced. Initially pioneered by Manasevit in the 1960s [102], the process is based on the release and subsequent pyrolysis of precursors, such as hydrides or metalorganic compounds containing group V and group III elements, as well as dopants. Operated at elevated temperatures, typically ranging from 600 to 700°C, the cracked precursors diffuse onto the substrate surface, where they undergo epitaxial growth, integrating seamlessly into the newly formed solid layers.

Normally, the precursors are transported by a carrier gas, commonly purified hydrogen (H_2), facilitated by a palladium membrane. MOVPE can be executed under both atmospheric pressure and low-pressure conditions (around tens and hundreds of mbar), with the latter often preferred, as practiced at IES-UPM. Low-pressure conditions offer several advantages, including minimizing the occurrence of unwanted gas-phase reactions that could introduce impurities into the epitaxial layers. Additionally, operating under reduced pressure enhances the mean free path of gas molecules, facilitating mass transport and affording greater control over growth rate and thickness uniformity, crucial factors in epitaxial layer deposition.

One of the most appealing aspects of this method lies in its capacity to achieve high growth rates, reaching from a few to some tens of $\mu m/h$, without compromising crystal quality. Additionally, the gas-phase deposition enables simultaneous growth on multiple substrates, enhancing efficiency and scalability. However, realizing such high-quality films necessitates meticulous control over various parameters, including temperature, precursor decomposition efficiency, gas flow rates, substrate surface quality, among others. Moreover, the use of

precursors comes with its own set of challenges, as they tend to be costly, toxic, and volatile, underscoring the importance of stringent safety measures and handling protocols in the deposition process.

This brief overview of the MOVPE context aims to provide a foundational understanding, acknowledging its inherent complexity, which exceeds the scope of this Thesis. Interested readers are directed to additional resources [103] for a comprehensive exploration. It is worth noting that III-V materials deposited on Ge/Si virtual substrates were produced using the MOVPE method. As previously indicated, the deposition of Ge onto Si was accomplished using the RF-PECVD technique by LPCIM (Paris). Detailed technical specifications of this method are referenced elsewhere [104]. Further elaboration on this method is omitted here, as our focus in this work lies more on its characterization for the purpose of understanding its application in solar devices.

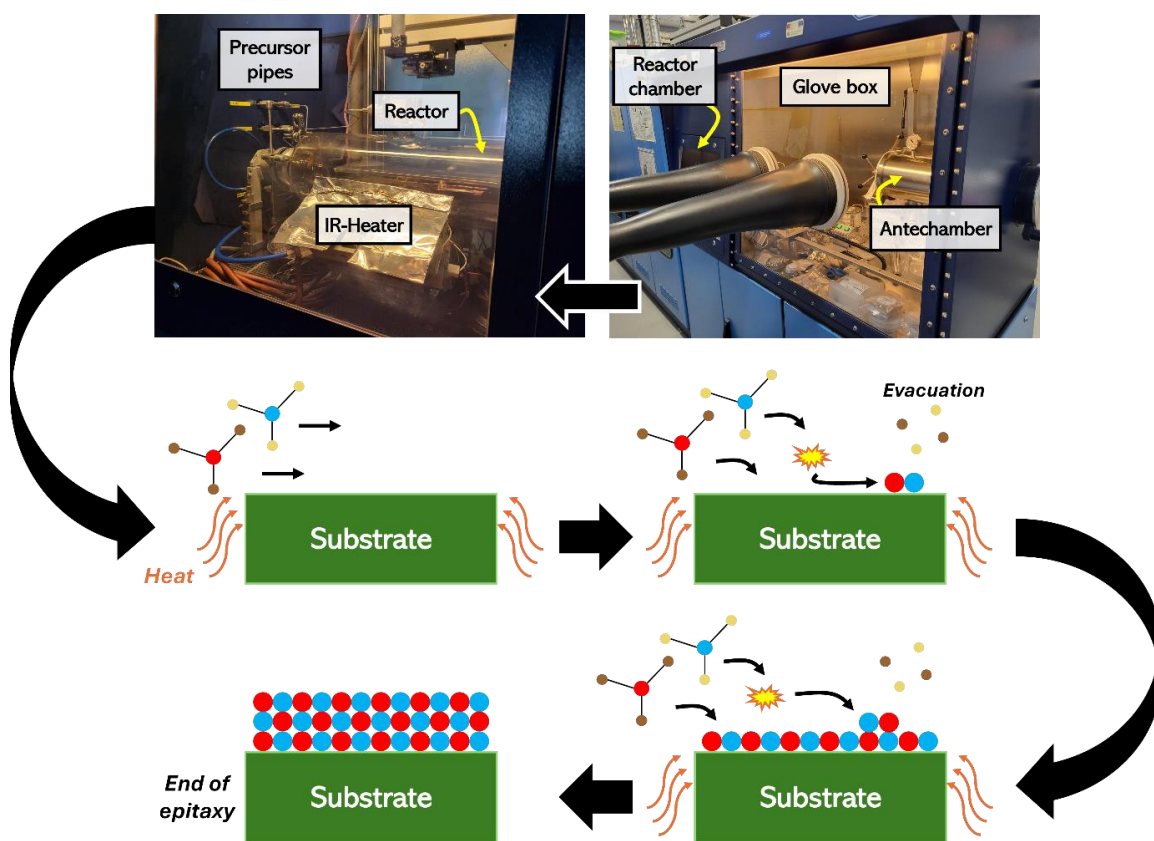


Figure 2.1. Sequential steps of a MOVPE process at IES-UPM. The substrate enters the reactor from the glove box, where it is warmed by the IR-Heater while precursors are introduced. These precursors undergo cracking, depositing desired atoms (blue and red circles) onto the substrate while byproducts (yellow and brown circles) are evacuated. This cycle continues until the desired layer/s are fully deposited, ready to be extracted from the MOVPE system.

At IES-UPM, epitaxial growth processes, both those discussed in the preceding sections and those undertaken in this Thesis, are conducted using a horizontal, research-scale MOVPE

reactor (AIX200/4). In the initial stage of the deposition process, the substrate is transferred from the antechamber to the glove box environment. Prior to this transfer, the antechamber undergoes a nitrogen gas (N_2) purge to minimize any potential contamination within the inert atmosphere of the glove box, which is also maintained under a nitrogen atmosphere. The reactor chamber is opened and the substrate is carefully positioned on a graphite susceptor capable of accommodating wafers with diameters of 2 and 4 inches. Prior to beginning the epitaxial growth process, the reactor chamber is securely sealed using an O-ring mechanism integrated into the hatchway. The satellite mechanism within the reactor initiates rotation to facilitate uniform epitaxial growth across the substrate surface. The transportation of precursor molecules is facilitated by high-purity hydrogen gas (H_2), which acts as the carrier gas. Additionally, an IR-heater is employed to elevate the temperature of the susceptor and the wafer to the desired level, thereby initiating the epitaxial growth process. The available precursors in our MOVPE reactor include hydrides, namely arsine (AsH_3) and phosphine (PH_3), as well as metalorganic compounds, namely trimethyl gallium (TMGa), trimethyl indium (TMIn), trimethyl aluminum (TMAI), dimethyl zinc (DMZn), diethyl telluride (DETe) and di-tert-butylsilane (DTBSi) and the precursor carbon tetrabromide (CBr_4). Of these, the latter four metalorganic precursors serve as typical dopants, with zinc (Zn) and carbon (C) acting as p-type dopants, and Si and tellurium (Te) serving as n-type dopants for III-V materials. Upon completion of the deposition process, the sample is retrieved from the reactor through a reversal of the initial path, traversing from the reactor to the glove box and then to the antechamber. This MOVPE sequence is depicted schematically in Figure 2.1.

2.1.2 In-situ Reflectance Anisotropy Spectroscopy

In our MOVPE reactor, the availability of an in-situ characterization tool (EpiRAS 2000) provides valuable perspectives into the quality of sample surfaces in real-time. Although not extensively detailed in this subsection, the inclusion of this method aims to facilitate a better comprehension of the measurements conducted on the samples within this Thesis, with further elaboration available elsewhere [105]. RAS is a non-destructive optical probing method capable of operating across diverse environmental conditions. Essentially, RAS quantifies the difference in reflectance (Δr) of plane-polarized light at normal incidence between two orthogonal directions in the surface plane (x, y), normalized to the mean reflectance (r):

$$\frac{\Delta r}{r} = 2 \frac{r_x - r_y}{r_x + r_y} \quad \text{Eq. 2.1}$$

where the reflectance r corresponds to the complex Fresnel reflection amplitudes. Optical probes, in general, exhibit limited surface sensitivity as they penetrate multiple atomic layers into the bulk of materials considered 'opaque' to such measurements. However, materials with a cubic crystal structure, such as diamond or zinc blende structures found in IV and III-V materials, respectively, exhibit isotropic bulk linear optical responses under normal incidence light, where $r_x = r_y$. In such scenarios, any observed anisotropic reflectance stems primarily from surface effects or non-linear phenomena, typically negligible in RAS measurements. RAS serves as a potent tool for measuring anisotropy across various systems. For instance, anisotropic configurations of an isotropic material aligned uniformly on an isotropic substrate can elicit an RAS signal. Although RAS has predominantly probed single crystal surfaces in published research, advancements in interpreting RA spectra can be coupled with complementary characterization techniques like STM or LEED, among others.

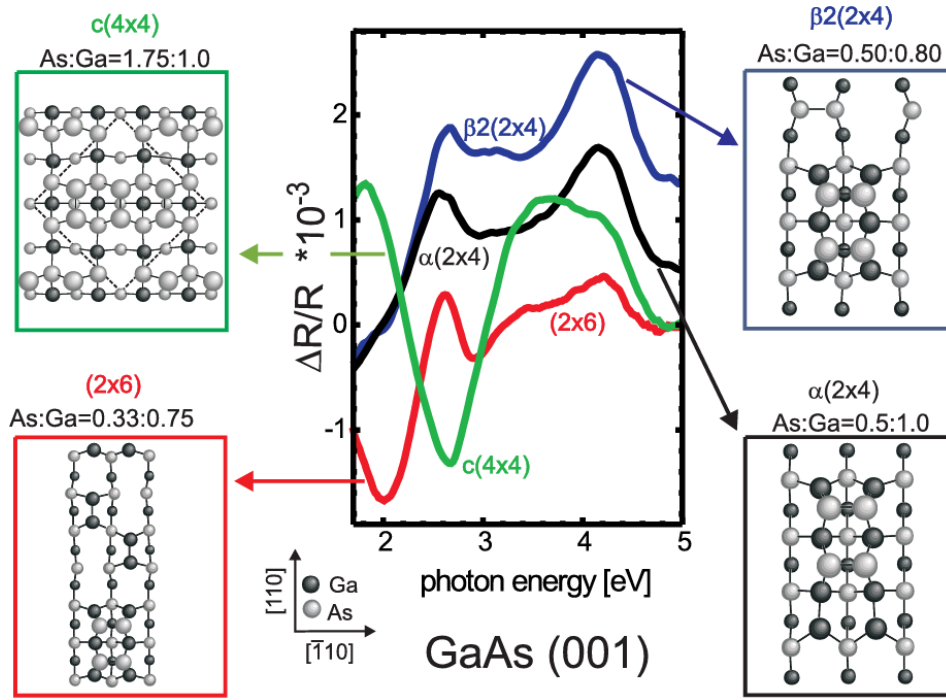


Figure 2.2. RAS spectrum for various GaAs (001) surface reconstruction. This figure was sourced from [106].

In the semiconductor epitaxy field, this method has proven effective, especially in early RAS studies centered on GaAs surfaces, for those oriented along (001) [106], [107]. Illustrating this usefulness, Figure 2.2 presents an exemplary RAS signal plotted against the GaAs (001) surface reconstruction, delineating the arrangement of surface atoms. The scrutiny of surface morphology, a pivotal aspect across all epitaxy systems, assumes paramount importance as it dictates growth mechanisms and ultimately impacts the quality of the overlying deposited layer. As mentioned, the combination of RAS with LEED and STM has revealed its utility,

highlighted in research exploring the characteristics of P-rich and Ga-rich GaP(001) surfaces [108]. Recognizing its reliability and acknowledging the logistical challenges of integrating multiple measurements for comprehensive analysis of RAS signals, this Thesis adopts a qualitative approach. The analysis in Sections 3.1 and 4.1. is primarily comparative, leveraging signal comparisons to assess surface quality, further supported by insights gained from prior work investigating GaInP deposition on Ge substrates [88].

2.1.2.1 In-situ reflectivity

As previously mentioned, the reflectance in RAS is modulated by the difference in the reflectance of polarized light in perpendicular planes ($r_x - r_y$ as described in Eq. 2.1). However, it is also feasible to conduct reflectance measurements without this modulation, which is referred to as the DC signal. The DC signal represents the average reflectance of the incident polarized light ($(r_x + r_y)/2$ in the denominator of Eq. 2.1) and is influenced by the overall surface properties, including composition, roughness, and cleanliness.

The DC signal serves as a reference level for RAS measurements. Given that RAS measures the differential reflectance between two orthogonal polarization states, maintaining a stable and accurate DC signal is crucial to ensure that these differential measurements are properly referenced. The DC signal thus acts as an indicator of surface condition. It provides critical information about the overall reflectivity properties of the surface, which can be affected by factors such as surface roughness, contamination, and the thickness of surface layers. Analyzing variations in the DC signal helps in understanding the general condition and cleanliness of the surface.

An illustrative example is provided in [109], where the DC reflectance of surfaces processed with various chemical methods was analyzed to assess surface quality for epitaxial purposes. This was achieved using the transient mode, which involves measurements at a constant photon energy. In our in-situ measurements, an energy of 2.1 eV is selected as it has demonstrated the best signal in our setup.

Another key feature of RAS is its capability to measure several important parameters of epitaxial growth, such as the GR of thin films [110] and their thickness. This is made possible by Fabry-Perot oscillations, which result from the interference of light reflected from the top and bottom surfaces of the thin film. These interferences can be either constructive or destructive, altering the signal intensity detected by the EpiRAS. The intensity of the reflected light is influenced by the thickness of the growing layer d , the optical constants of the material, and the wavelength of the incident light. Constructive and destructive interferences correspond to maximum and minimum reflectance, occurring at:

$$2nd_{max} \cos(\alpha) = m\lambda \quad \text{Eq. 2.2}$$

$$2nd_{min} \cos(\alpha) = (m + 1/2)\lambda \quad \text{Eq. 2.3}$$

where m is the order of interference, an integer value, n is the refractive index of the film, and α is the angle of incidence of the light.

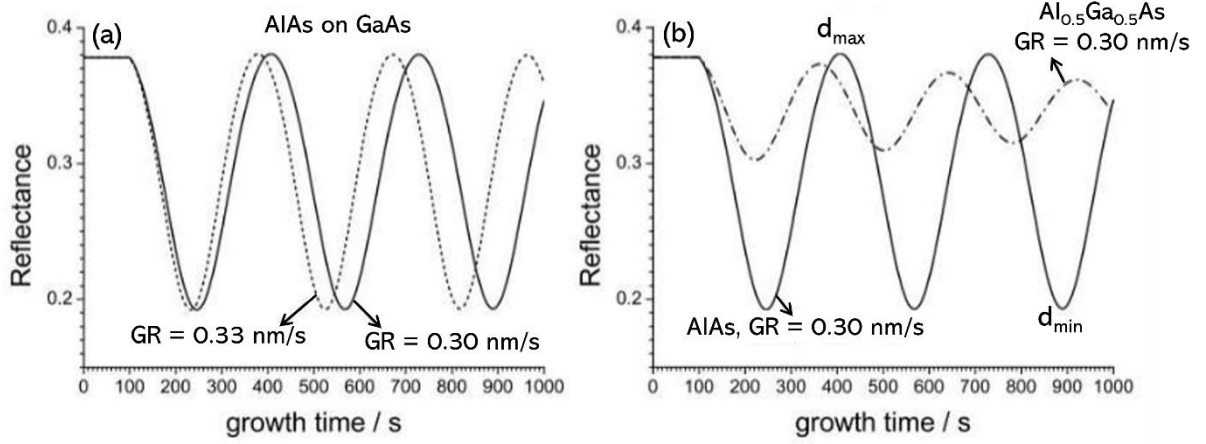


Figure 2.3. Reflectance graphs for AlAs-based deposition on GaAs. (a) Illustration of the change in the period with varying GR. (b) Illustration of the change in signal intensity and period as the Ga content increases in the ternary AlGaAs alloy. The labels d_{max} and d_{min} indicate the points of maximum and minimum interference, respectively. (Source: Information notes of www.laytec.com)

During epitaxial growth, the reflectance pattern is continuously recorded over time in transient mode, showing the aforementioned maxima and minima peaks, as illustrated in Figure 2.3(b). The EpiRAS tool utilizes these peaks to determine the thickness of the film through specialized equipment and optical calculations based on the Fabry-Perot oscillations, taking into account the continuous growth of the film. By analyzing the periodicity and shifts of the Fabry-Perot oscillations in the reflectance spectrum over time, the GR can be calculated by considering the time interval between peaks. Once the GR is obtained, the film thickness can be easily determined by multiplying the GR by the duration of the deposition.

Even with these simple considerations, which account only for reflectance minima and maxima, illustrate how different process parameters affect reflectance. In a comparative view, higher GR results in a shorter period of oscillations, enabling the identification of different GRs in the same material, as shown in Figure 2.3(a). Additionally, since the refractive index is a factor in the analysis, changes in film composition can be detected. For example, the Ga content in a ternary $Al_xGa_{1-x}As$ alloy can be determined (Figure 2.3(b)), since the change in refractive index is known.

As will be discussed in Sections 3.1 and 4.1, this method was employed to determine the surface quality of both Ge and Ga(In)As surfaces. The analysis was conducted through a combination of energy scans and the transient mode.

2.2 Epitaxial material characterization techniques

2.2.1 Electrochemical capacitance-voltage

The ECV measurement is probably the most used technique to measure doping profiles. It basically consists of measuring the depletion capacitance of an electrolyte/semiconductor junction and extracting the carrier concentration of the semiconductor from that voltage. In addition, the electrolyte can be used to etch the semiconductor in successive steps and a controlled way, enabling the measurement of doping profiles. The schematic representation of the characterization setup is depicted in Figure 2.4(a).

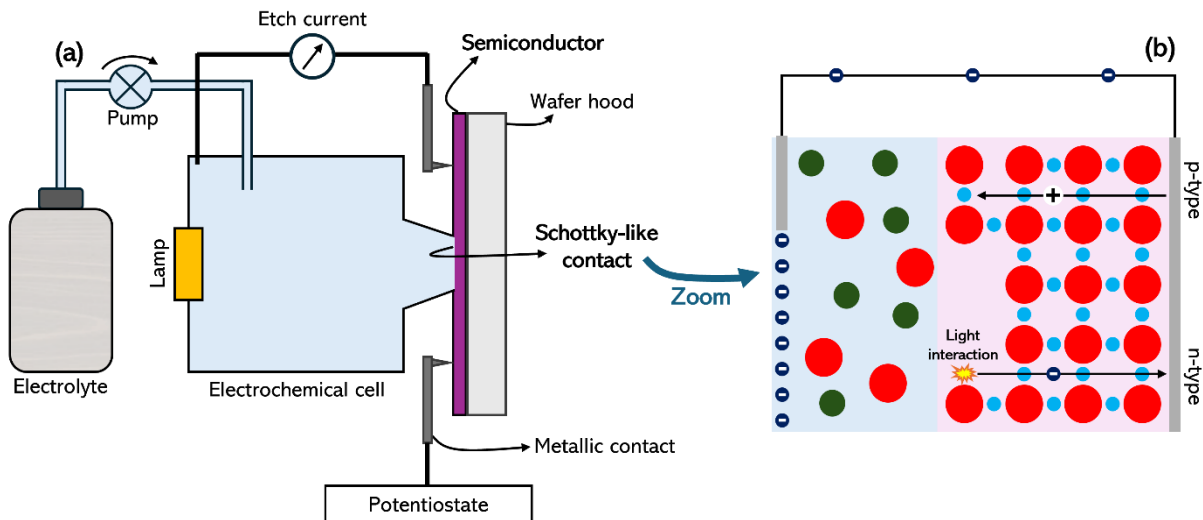


Figure 2.4. (a) Schematic illustration of the ECV measurement method with labeled components. (b) Representation of the etching process in ECV, depicting the procedure in p-type (upper half) and n-type (lower half) semiconductors. Blue circles denote electrons, white circles represent holes, red circles depict component atoms in the sample, and green circles denote atoms from the electrolyte.

An electrolyte, supplied from a reservoir, is housed within the electrochemical cell. The semiconductor sample, sealed with an O-Ring, rests on this cell, allowing direct contact between the electrolyte and the semiconductor surface. Positioned on a wafer hood are two metallic contacts that make contact with the semiconductor surface. These contacts facilitate the control of current and potential, thereby influencing the etching rate and affecting the semiconductor surface. Consequently, this measurement process is inherently destructive, rendering the sample unsuitable for further analysis thereafter. The procedure for measuring n-type and p-type materials differs: under reverse bias, the concentration of ionized donors and acceptors can be assessed. This contrast is illustrated in Figure 2.4(b). For p-type

materials, holes may be conducted from the semiconductor contact to the surface, where they can release valence electrons of the p-type semiconductor surface atoms through recombination. Once all valence electrons of a semiconductor atom are extracted, the positively ionized atom core dissolves into the electrolyte. In contrast, for n-type materials, light may be utilized to generate electron-hole pairs at the semiconductor surface. If these holes diffuse to the surface, facilitated by the intrinsic electrical field of the semiconductor/electrolyte interface, they may release valence atoms of the n-type semiconductor surface atoms through recombination. The liberated electrons are then conducted to the semiconductor contact, leading to the dissolution of positively ionized atoms into the electrolyte upon removal of valence electrons.

The Schottky barrier established at the electrolyte-semiconductor interface has a depletion region associated with it, with a width described by assuming the barrier behaves like a capacitor with plane-parallel plates. Thus, the capacitance can be expressed as:

$$C = \frac{A\epsilon_0\epsilon_r}{W} \quad \text{Eq. 2.4}$$

Subsequently, following a plane-parallel capacitor model, the determination of concentration values is facilitated through C-V measurements, where capacitance is, in this case, defined as:

$$C = -\frac{dQ}{dV} = q \cdot A \cdot N \cdot \frac{dW}{dV} \quad \text{Eq. 2.5}$$

By differentiating Eq. 2.4 with respect to Eq. 2.5, the indirectly measured carrier concentration is determined as:

$$N = \frac{-2}{q\epsilon_0\epsilon_r A^2 \frac{d(1/C^2)}{dV}} \quad \text{Eq. 2.6}$$

Hence, the slope of the $1/C^2$ -V curve becomes instrumental in discerning the type of doping and identifying the carrier charges. This slope is typically selected near the voltage that aligns the band of the Schottky barrier with that of the semiconductor [111], where the etching is optimal due to the absence of a barrier.

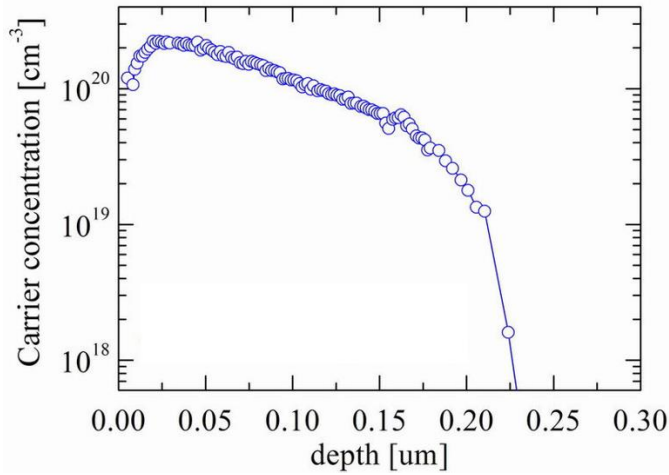


Figure 2.5. Carrier profile (p-type) resulting from boron diffusion into Si. As referenced in [112], this profile denotes the emitter region of the solar cell under investigation.

Such measurements offer insights into the profile of active carriers [113], [114], aiding in the determination of emitter and base thickness in solar cells. A pertinent example is provided in [112], where a multicrystalline p⁺n Si solar cell was engineered with boron diffusion into Si. Figure 2.5, derived from the present investigation, depicts a typical ECV profile, where an estimation of the emitter thickness at approximately 200 nm. Furthermore, they can indicate significant changes in the dopant profile, albeit unable to capture the chemical profile within the bulk. Nonetheless, these measurements provide an initial overview of dopant diffusion changes, presuming that the majority of carriers are contributed by the dopant.

Epitaxial III-V layers are normally very uniform in depth. Thus, the ECV technique is used to ascertain the actual doping level of the layer. However, sometimes the doping uniformity can be affected by unwanted diffusion of dopants during the growth of the remainder of the structure. In this case, the ECV profiling becomes crucial. Another case of central interest to this Thesis is the formation of Ge junctions. Each Ge cell sample discussed in this Thesis incorporates a GaAs-based layer, consisting of either GaAs or GaInAs with an approximate indium content of 1%, deposited on Ge. These Ge substrates may either be standard Ge substrates or Ge previously deposited on silicon (referred previously to as ultra-thin Ge|Si virtual substrates). As will be explained in Chapter 5, the Ge junction form by diffusion of the constituents of the III-V layers into the Ge substrate, producing a characteristic diffusion profile.

It is also important to note that sometimes the ECV measurements require some pre-processing of the semiconductor structures, to gain access to the layer that is to be characterized. Although the ECV allows etching through the structure, doing so across heterojunctions is normally problematic and is avoided. For example, should there be a need to measure carrier profiles within the Ge bulk, it becomes necessary to remove the deposited GaAs layer while retaining the underlying Ge layer. To achieve this, a mixture of phosphoric

acid (H_3PO_4) and nitric acid (HNO_3) in a 3:1 ratio has been chosen due to its high selectivity towards Ge while exhibiting aggressive etching properties towards GaAs-based layers [115]. Finally, the carrier profiles were assessed using the WEP CVP 21 tool housed in our laboratory. Notably, the Ge process was facilitated using Tiron as the electrolyte, which was indicated for this type of material as indicated by the ECV designer.

2.2.2 Atomic force microscopy

AFM are valuable tools for evaluating nanoscale surface metrology and material properties of samples. Unlike conventional compound optical microscopes, which are subject to the limitations of visible light wavelengths, AFMs offer superior resolution. While optical microscopes have a maximum magnification of approximately 1000x, resulting in a resolution of around a few tens of a μm , AFMs transcend these limits and enable the differentiation of points at distances of nanometers. This achievement is attributed to AFM's distinctive non-optical surface technique, which is based on the principles of scanning probe microscopy. By utilizing a physical probe to meticulously scan and measure surface features, AFMs provide atomic resolution for both lateral and height measurements, thereby unveiling details of nanoscale structures.

AFM microscopes function on the principle of surface sensing, employing an ultra-sharp tip mounted on a micromachined probe. This tip traverses the sample surface in a raster pattern, scanning line by line, as depicted in Figure 2.6. Fundamentally, AFM operates by attaching a nanoscale tip to a small cantilever, forming a spring-like mechanism. When the tip interacts with the surface, the cantilever bends, and this bending is detected using a laser diode and split photodetector. The degree of bending reflects the force of interaction between the tip and sample, allowing for the measurement of cantilever deflections as small as a few Å [116]. The chosen operational mode for our experiments was tapping mode, which minimizes contact between the tip and sample to prevent damage. In this mode, the cantilever vibrates near its resonance frequency, causing the tip to execute a sinusoidal motion. This motion is altered by attractive or repulsive interactions as the tip approaches the sample. A feedback loop, akin to that used in contact mode, is employed to maintain a constant tapping amplitude rather than quasi-static deflection. An illustrative case of this measurement type is presented in the study of GaInP layers deposited on Ge substrates [117]. Figure 2.7 shows two defect types identified in GaInP: the arrowhead (a) and the asymmetric inverted pyramid (b). AFM analysis and complementary measurements revealed that the formation of the pyramidal defects is independent of the layer composition, whereas the density of arrowhead defects increases with a higher Ga content in the layer.

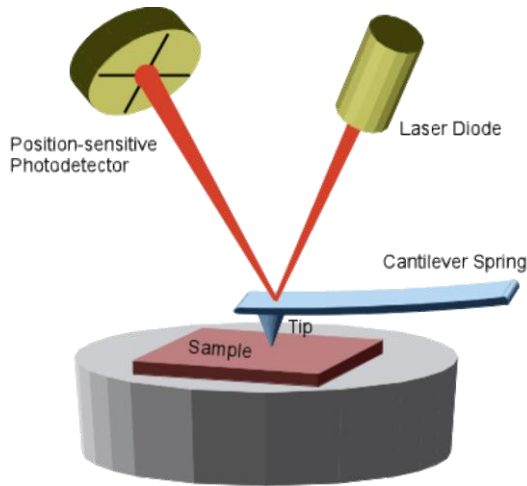


Figure 2.6. AFM measurement representation. The AFM tip scans the sample surface, inducing a slight deflection in the cantilever. This deflection alters the laser reflection, translated into an intensity map by the detector. (Source: <https://physik.uni-greifswald.de/en/research-groups/soft-matter-and-biophysics-prof-christiane-helm/methods/afm-atomic-force-microscope/>)

The surface characteristics of the selected samples were examined utilizing the Park XE-10 AFM Microscope, situated at *Universidad Carlos III (Leganés)* in the *Departamento de Física Aplicada*. This analytical approach proves invaluable as surface roughness impacts the efficiency of solar cells, chiefly due to non-desirable recombination phenomena occurring at heterointerfaces [118]. In this Thesis, this technique has been employed to evaluate the surface quality of Ge/Si samples and the epitaxially deposited III-V materials, as detailed in Sections 3.3.1 and 3.4.1, respectively. Additionally, it has been used to assess surface roughness for investigating arsenic diffusion into standard Ge substrates, as discussed in Section 5.5.1.1.

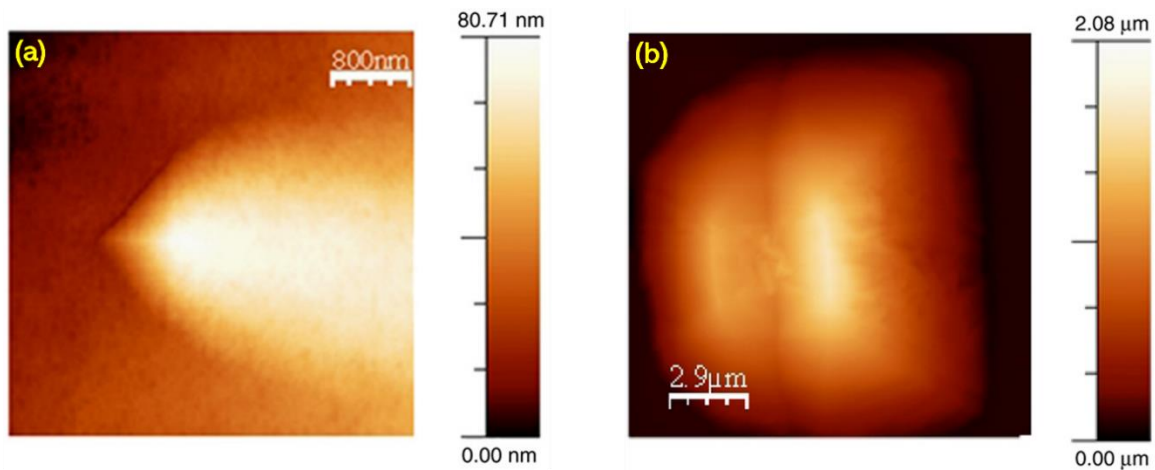


Figure 2.7. AFM images of defects formed on GaInP deposited on a Ge substrate: (a) arrowhead defect and (b) asymmetric inverted pyramid defect. These images are sourced from [19].

2.2.3 Transmission electron microscopy

The following characterization techniques are incorporated within TEM. Prior to detailing these methods, a brief introduction to TEM is presented to provide foundational understanding.

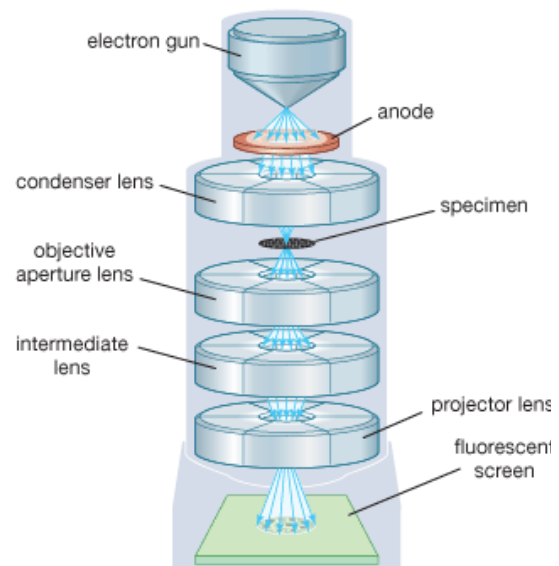
TEM is a powerful technique in microscopy, offering unparalleled insights into materials at the atomic and nanoscale levels. Operating on the principle of transmitting an electron beam through an ultra-thin specimen, typically hundreds of nanometers thick, TEM capitalizes on two essential features: its remarkable lateral spatial resolution and its unique ability to provide both imaging and diffraction capabilities. This method serves as a powerful tool for elucidating the comprehensive morphological, crystallographic, and atomic structural characteristics of diverse materials.

At the core of TEM lies the utilization of an electron beam to visualize the specimen. Positioned at the top of the microscope, the electron gun emits electrons that traverse through a vacuum tube, engineered to prevent unwanted collisions with airborne particles. Employing electromagnetic lenses, the instrument precisely focuses the electron beam to a fine point as it traverses the ultra-thin specimen. Upon passing through the specimen, the transmitted electrons hit upon a fluorescent screen located at the microscope's base, forming an image that delineates various features of the specimen based on their respective densities. The schematic representation of the TEM working principle is depicted in Figure 2.8.

Figure 2.8. Schematic representation of a transmission electron microscope, illustrating its components.

(Source:

<https://www.britannica.com/technology/transmission-electron-microscope>)



The resulting TEM image is a manifestation of the specimen's intricate structure, with regions of differing atomic numbers or thicknesses exhibiting different levels of electron beam attenuation. High atomic number or thick regions absorb a greater portion of the electron beam, resulting in reduced signal intensity and darker regions in the image. Conversely, areas with lower atomic numbers or thinner regions permit greater electron transmission, yielding brighter features in the image. Through the phenomena of scattering and diffraction, TEM can provide insights into the spatial arrangement of atoms within the bulk material, as well as invaluable information regarding the material's chemical composition and electronic structure.

In epitaxies for solar applications and other applications in electronics, TEM serves as a versatile tool offering multifaceted insights. One primary application lies in crystal structure analysis, wherein TEM facilitates the meticulous examination of epitaxial layers, elucidating critical parameters such as lattice parameters [119]. Moreover, TEM proves indispensable in defect analysis, proficiently identifying and characterizing imperfections within epitaxial layers like dislocations [120]. As discussed in section 1.2.3, the significant lattice mismatch between Si and GaAs leads to the formation of TDs. These TDs can self-annihilate upon encountering each other, a process that can be enhanced by annealing, which supplies the necessary energy for TD movement. In reference [121], this concept was applied, and, as illustrated in Figure 2.9, annealing at higher temperatures leads to a more significant reduction in TDD within the dislocation filter structure composed of GaAs and GaInAs/GaAs (* in the figure). Additionally, interface characterization with TEM enables researchers to scrutinize the interfaces between disparate epitaxial layers or between the epitaxial layer and its substrate. This investigative avenue encompasses the evaluation of interface sharpness or the identification of interfacial defects [122]. Within this Thesis, particular emphasis is placed on interface characterization to delve into the aspect and sharpness of the sample, unravelling potential effects and defects arising from the epitaxy, particularly in our GaAs/Ge heterointerfaces in Section 3.3.1. The measurements were carried out using the ELECM facilities, particularly the Talos F200X (S)TEM model located at the *Universidad de Cádiz*.

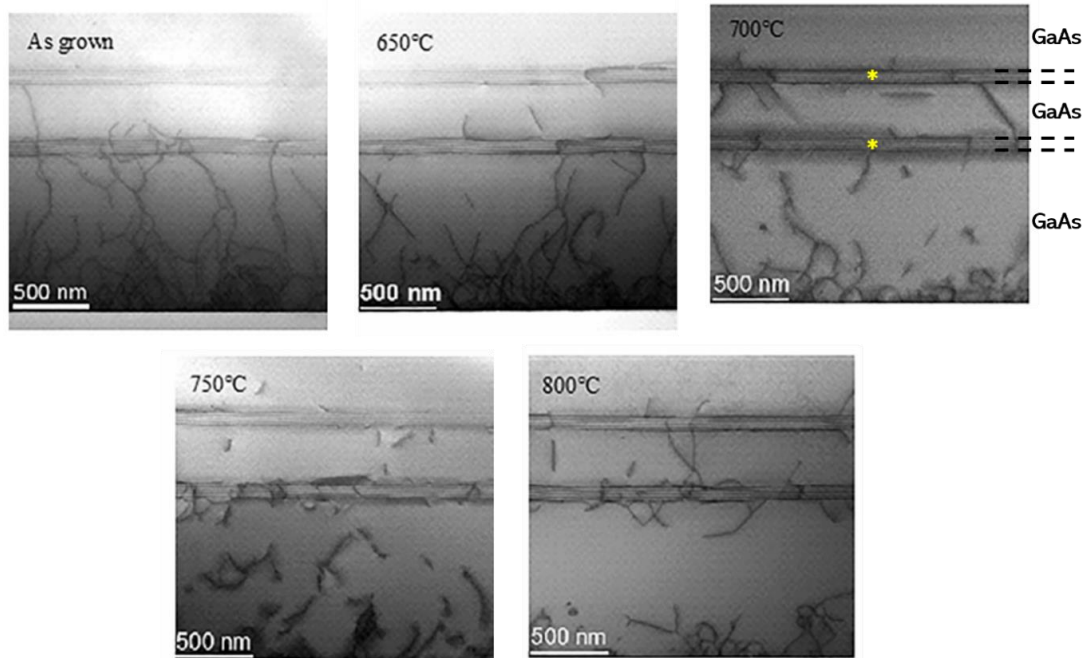


Figure 2.9. Cross-sectional TEM images illustrating the reduction of TDD with increasing annealing temperature (indicated in the upper left corner of each image). Yellow asterisks denote a thin film of GaInAs/GaAs within the GaAs dislocation filter. Images are sourced from [121].

2.2.3.1 High-resolution transmission electron microscopy

HRTEM is a variant of TEM imaging characterized by magnifications sufficient to resolve lattice spacings of inorganic materials, typically in the range of several angstroms. The fundamental principle of HRTEM involves the interaction between a highly focused electron beam and the specimen. Electrons, accelerated to high energies, are transmitted through an ultra-thin specimen. Preparing specimens for HRTEM involves making them thinner than standard TEM specimens to ensure electron transparency, while striving to preserve their native structure despite potential damage from the high-energy electron beam. As the electrons traverse the sample, they are scattered by the electrostatic potential of the atoms, generating a diffraction pattern that is subsequently magnified to produce an image.

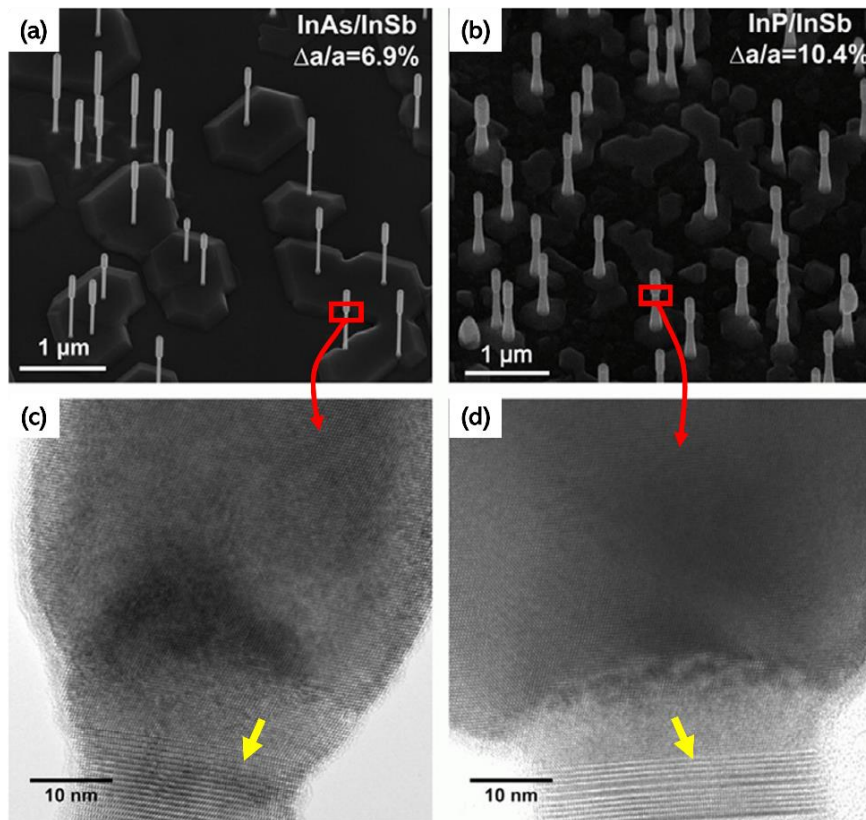


Figure 2.10. SEM images of InSb nanowires after deposition of InAs (a) and InP (b) materials. HRTEM micrographs highlight the interfaces between these materials ((c) for InAs and (d) for InP). Yellow arrows indicate the disruption of atomic arrangements at the interfaces. Images are sourced from [123].

HRTEM achieves atomic resolution through the utilization of coherent electron waves. These waves interact with the crystal lattice, undergoing constructive and destructive interference, thereby forming a high-resolution image that accurately depicts the periodic structure of the specimen. This interference pattern, known as phase contrast, enables the direct visualization of atomic columns in crystalline materials. In the field of material sciences, HRTEM is

indispensable for a variety of applications, including determining the atomic structure of materials, elucidating crystal defects, and investigating phase transformations, interface structures, and dislocation dynamics.

An illustrative application in semiconductor research involves the investigation of interfaces between various III-V materials deposited on InSb nanowires [123]. As depicted in Figure 2.10, these nanowires exhibit different features alongside the deposited materials, highlighting lattice mismatches in the upper right corners of panels (a) and (b) as seen in the SEM images. The interfaces visibly disrupt the atomic arrangement, which is evident from the clear delineations marked by yellow arrows in panels (c) and (d) shown in HRTEM images. In Section 3.3 of this Thesis, HRTEM has been similarly employed to identify dislocations at Ge|Si interfaces.

2.2.3.2 Bright-field transmission electron microscopy

BF-TEM and BF-STEM represents essential modalities within electron microscopy. Unlike conventional TEM, where the electron beam illuminates a wide area of the specimen, STEM focuses a finely localized beam that scans across the sample in a raster pattern. Both techniques rely on directing a coherent and accelerated electron beam through an ultra-thin specimen, facilitating detailed imaging and analysis of material structures at microscopic scales. Electrons interact with the atomic potential of the material as they traverse it. BF-TEM selectively captures unscattered, which are then collected by an objective lens and focused onto an imaging plane. This process generates a high-contrast image that reveals variations in sample thickness, density, and composition. Darker areas in the resulting image correspond to regions of higher atomic number or thickness, reflecting greater electron scattering and absorption.

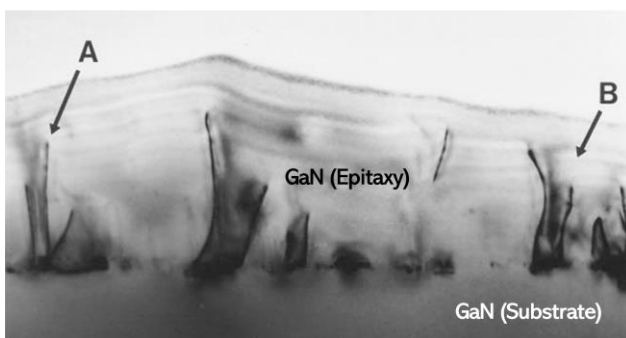


Figure 2.11. BF-TEM image showing epitaxially deposited GaN on a GaN/sapphire substrate. Examples of dislocations are highlighted by arrows labeled as A and B. Image is sourced from [124].

In material science, BF-TEM proves highly effective in revealing the crystallographic structure of materials. Analysis of contrast variations and diffraction patterns in BF-TEM images facilitates determination of lattice parameters, identification of crystallographic defects, and exploration of phase transformations with exceptional precision and detail. An exemplifying

instance of its utilization is found in the investigation of dislocations in epitaxially grown GaN on GaN/sapphire substrates [124]. Figure 2.11 displays dislocations observed in the deposited GaN, with specific examples marked by black arrows and labeled with corresponding letters. Section 3.3 of this Thesis employs BF-TEM similarly for identifying dislocations at Ge|Si interfaces.

2.2.3.2.1 Annular bright-field imaging

ABF imaging is a technique derived from STEM. In contrast to conventional bright-field imaging, which collects unscattered electrons to form an image, ABF imaging employs an annular detector positioned to collect electrons scattered at small, yet specific, angles.

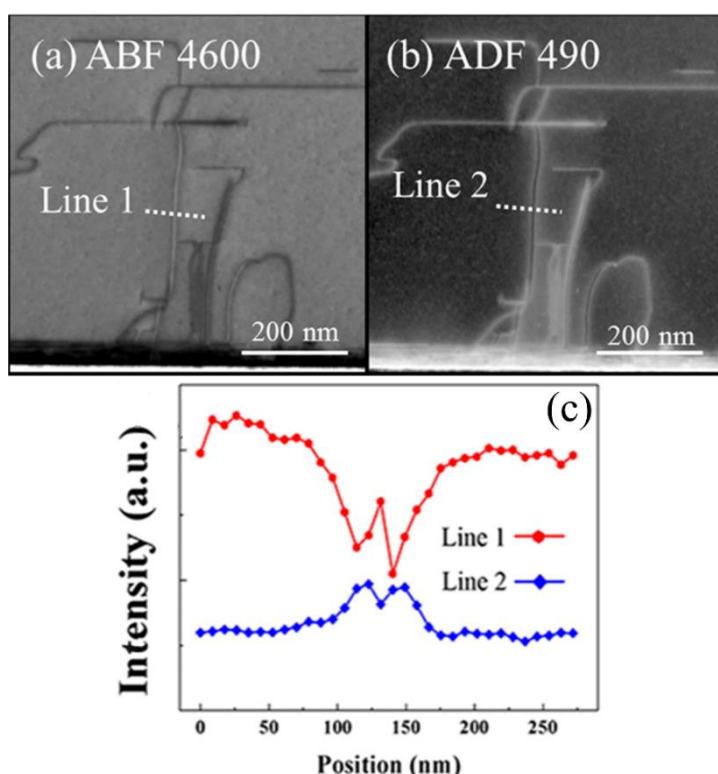


Figure 2.12. (a) ABF-STEM image and (b) ADF-STEM image of GaN deposited on sapphire. (c) Intensity profiles obtained from the lines indicated in the images above. The upper tags denote the camera length in millimeters. Images are sourced from [125].

In ABF imaging, when the focused electron beam encounters a defect, the local atomic arrangement is disrupted. This alteration in structure influences the scattering angle of the electrons. Defects scatter electrons differently compared to the perfect crystal lattice, resulting in distinctive contrast in the ABF image. This contrast enables to directly visualize and analyze atomic-scale defects. Thus, ABF imaging facilitates the detailed study of crystal defects, interface structures, and the effects of atomic-scale perturbations on material behavior. Figure 2.12(a) presents an ABF-STEM image of GaN epitaxially deposited on sapphire

using MOVPE, highlighting various defects as part of a comprehensive study employing multiple TEM-based techniques for defect identification [125]. Figure 2.12(c) below illustrates the intensity profile along the line indicated in the upper images, showcasing the different characteristics of the TEM-based method used. In this thesis, this methodology has been applied to identify defects in RF-PECVD grown Ge on Ge substrates, as detailed in Section 3.3.

2.2.3.3 Annular dark-field imaging

Similar to bright-field imaging, previous to the explanation of the annular version, the generic technique must be introduced. DF-TEM operates on the principle of electron diffraction, wherein the incident electron beam interacts with the periodic atomic lattice of the specimen, resulting in diffraction patterns characteristic of the crystal structure. In contrast to BF-TEM, which utilizes the directly transmitted beam to form an image, DF-TEM leverages the electrons diffracted to specific angles. This is achieved by placing an aperture in the back focal plane of the objective lens to isolate and transmit only those electrons scattered by the crystalline planes of interest.

ADF imaging in STEM operates on principles akin to those of ABF imaging, where variations in the atomic structure influence the scattering angles of electrons. In ADF imaging, the annular detector is specifically designed to capture electrons scattered at high angles.

The detector selectively collects electrons that have undergone Rutherford scattering, which is the elastic scattering of charged particles due to the Coulomb interaction with nuclei. These scattered electrons can be detected based on the contrast generated by their different scattering behaviors, which vary due to the presence of defects within the material. By analyzing the intensity and distribution of these scattered electrons, ADF imaging can identify defects and elucidate compositional variations at the atomic scale. Figure 2.12(b) displays an ADF-STEM image of GaN epitaxially grown on sapphire using MOVPE, as referenced in section 2.2.4.2.1 [125]. Below, Figure 2.12(c) illustrates the intensity profiles along the indicated lines in the upper images, highlighting the different characteristics of ABF-STEM and ADF-STEM. This methodology has been utilized in this Thesis to identify defects in RF-PECVD grown Si on Ge substrates and III-V materials deposited on these Ge|Si virtual substrates, as discussed in detail in Sections 3.3 and 3.4, respectively.

2.2.4 Secondary ion mass spectrometry

SIMS instruments employ an internally generated beam of either positively charged ions (such as Cs) or negatively charged ions (such as O) as the primary beam. This primary beam is directed onto the surface of a sample to generate ions, which are then transferred into a mass

spectrometer across a high electrostatic potential, thus forming what are known as secondary ions.

The interaction between the primary ion beam and the sample, which occurs under vacuum conditions, provides sufficient energy to ionize many elements present in the sample. If the primary beam consists of positively charged ions, the resulting ionization process tends to favor the production of negative ions, whereas primary beams composed of negative ions tend to generate positive ions. While the majority of atoms and molecules removed from the sample surface by this interaction, a process known as sputtering, remain neutral, a certain percentage of these particles become ionized. These ions are subsequently accelerated, focused, and subjected to analysis by a mass spectrometer, as illustrated in Figure 2.13.

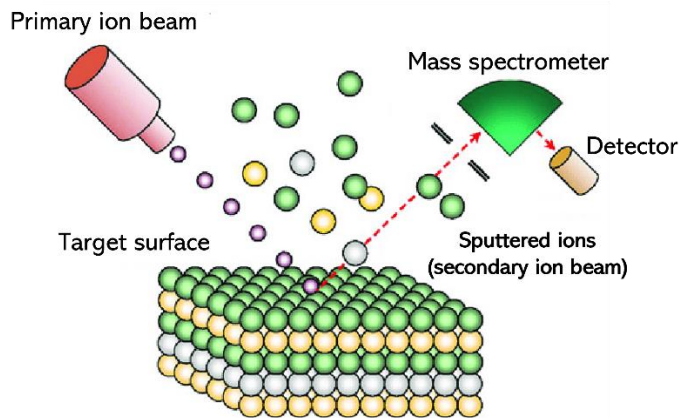


Figure 2.13. Schematic depiction of secondary ion mass spectrometry. Image source: [126].

The application of this characterization method has been extensive in the realm of epitaxy, particularly for investigating both intentional [127] and unintentional [128] doping within the bulk material. In contrast to the ECV technique, by SIMS the actual chemical composition is obtained. Therefore, the difference between SIMS and ECV profiles inform about effects such as compensation, partial activation of dopants, etc.

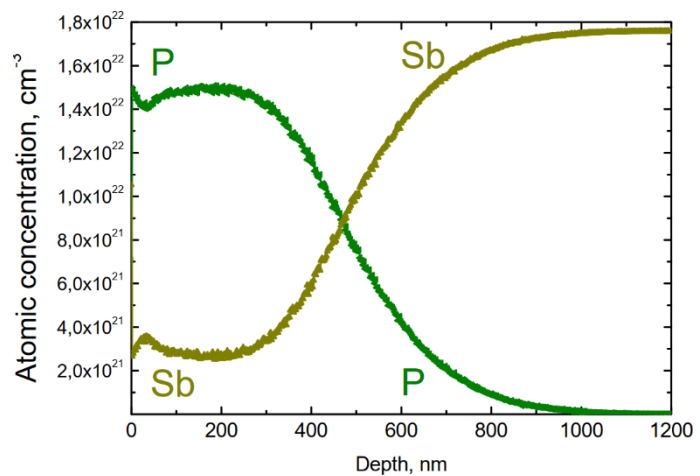


Figure 2.14. SIMS profiles of P and Sb vs. depth in $\text{GaP}_x\text{Sb}_{1-x}/\text{GaSb}$ structure obtained by processing GaSb in phosphorous vapors. The figure is sourced from [129].

For depth profiling to determine concentration variations along the material depth, dynamic SIMS is commonly employed. In this approach, the ion dose is sufficiently energetic to penetrate deeper layers of the material, allowing for the determination of composition as a function of depth. For illustrative purposes, Figure 2.14 [129] shows a SIMS profile with typical diffusion profiling. The study examined phosphorus diffusion into GaSb to form $\text{GaP}_x\text{Sb}_{1-x}$, aiming to achieve a wider bandgap suitable, e.g., for window layers in solar applications, via a solid-state substitution reaction method, eliminating the need for epitaxy. Phosphorus diffusion into GaSb is driven by exposure to phosphorus vapor at controlled temperatures.

In this study, SIMS profiles were obtained using a SIMS Cameca IMS 4f-E6 analyzer (RTG Mikroanalyse, Berlin) with a primary Cs^+ beam operating at 14.5 keV. As discussed in sections 5.5.1.2, 5.5.1.2.1, 5.5.2.2, 5.5.2.2.1, and 5.5.3 of Chapter 5, arsenic in germanium was the targeted element for analysis. Due to the challenge of separating the signals of ^{75}As and $^{74}\text{Ge}^1\text{H}$, the SIMS profiles exhibit a background signal, approximately $2 \cdot 10^{17} \text{ cm}^{-3}$, as a result of this analytical limitation.

2.2.5 Scanning electron microscopy

The subsequent two characterization techniques are integrated into SEM. Before explaining these methods, a brief introduction to SEM is provided to establish a basic understanding.

SEM serves as a usual tool in materials analysis, providing high-resolution images. Unlike optical methods, SEM employs a focused electron beam to examine specimen surfaces, yielding images with superior clarity. SEM instruments offer a resolution range down to less than 1 nm, surpassing the capabilities of traditional optical microscopes.

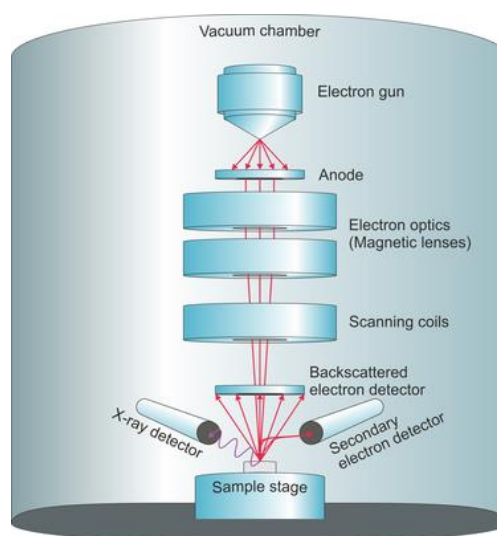


Figure 2.15. Schematic diagram illustrating the components of a scanning electron microscope. (Source: https://fakultaeten.hu-berlin.de/en/mnf/forschung_internationales/qrs/salsa/p-a-labs/application-lab/instrumentation/a-labs-sem)

The SEM process commences at the electron gun at the top of the machine, where electrons are generated and accelerated through the column at specific voltages, typically ranging from 1 keV to 30 keV. This controlled energy range allows electrons to penetrate varying depths into the sample. As the electrons progress down the column, condenser lenses and apertures work to narrow the beam diameter until it is focused onto the sample surface by the final lens. The scanning electron microscope then projects and scans a focused electron stream across the specimen's surface, collecting signals with specialized detectors. These signals, generated through interactions between the electron beam and the sample's atomic constituents, provide insights into surface topography and composition. Observation of acquired images is facilitated in real-time on external monitors, with software synchronizing the beam's position and detector intensity. This process enables researchers to uncover details of the sample's surface features with precision and accuracy. Figure 2.15 illustrates a schematic representation of this measurement device.

2.2.5.1 Electron channelling contrast imaging

ECCI is a recognized technique within the SEM imaging, leveraging the phenomenon of electron channeling relative to the crystallographic lattice planes. The contrast observed in ECCI images is intrinsically linked to the crystallographic orientation of the lattice within the specimen. When the crystal lattice aligns favorably with the electron beam, ECCI enables the visualization and characterization of individual dislocations within the sample, thereby furnishing information into slip systems and deformation mechanisms. Figure 2.16 serves as an illustrative representation of this principle. Detection of the resultant electron beam, stemming from its interaction with the channeling effect in the sample, is accomplished using a backscattered electron detector, as depicted in Figure 2.15, a standard component of SEM instrumentation.

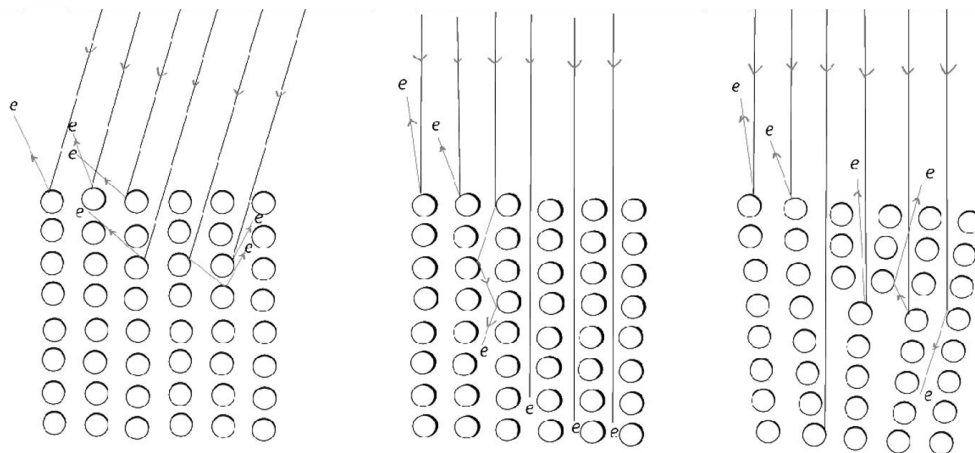


Figure 2.16. Various mechanisms of electron backscattering utilized by the ECCI method to generate contrast images. The image was acquired from [130].

In epitaxial growths for solar cell applications, ECCI has been a useful tool for the detection and characterization of threading dislocations (TD). Studies have utilized ECCI to examine the occurrence of such defects in various configurations, as outlined in the introduction, including the evaluation of TDD in GaP layers deposited on Si substrates [131], as well as investigations into TD within Ge buffer layers deposited on Si for future integration of III-V materials [132]. An ECCI image derived from the source previously cited [131] is presented in Figure 2.17. In this image, a notably high TDD of $4 \cdot 10^8 \text{ cm}^{-2}$ is evident due to the deposition of a GaAs layer onto a GaP/Si substrate characterized by an elevated pre-existing TDD. Consequently, prominent TD are discernible (yellow circles).

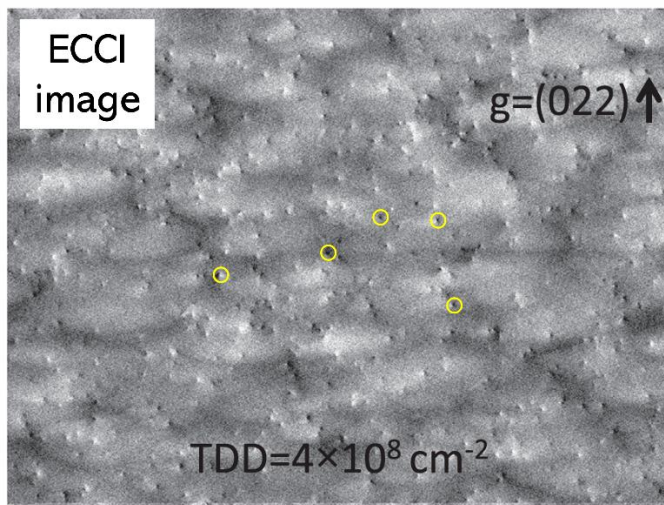


Figure 2.17. ECCI image of GaAs epitaxially grown on GaP/Si substrate with a previous high TDD. The calculated TDD from the image is provided in the lower part, with yellow circles highlighting select some of TDs. It was adapted from reference [131].

This Thesis aims to further explore the presence of TD in the provided Ge|Si virtual substrates grown using RF-PECVD, as discussed in Section 3.4. All measurements conducted using this technique were performed at the *Nanophotonics Technology Center, Universidad Politécnica de Valencia*, utilizing the Gemini SEM 500 FESEM and the Jeol IT800 SHL FESEM instruments.

2.2.5.2 Electron backscatter diffraction

EBSD is an adequate technique for characterizing the local crystal structure and orientation at the surface of a specimen. By collecting elastically backscattered electrons, which undergo coherent Bragg scattering upon exiting the specimen, EBSD provides discernments into the material's microstructure. A specialized EBSD detector captures the backscattered electrons over a wide solid angle, forming electron backscatter diffraction patterns characterized by Kikuchi bands [133]. These bands, illustrated in Figure 2.18, offer a visual representation of the crystallographic information encoded within the specimen. As demonstrated in (a) of the figure, the initial pattern corresponds to the Si(100) crystal orientation. However, upon rotation (b) or tilt (c) of the specimen, the Kikuchi bands shift accordingly, reflecting changes in crystal orientation.

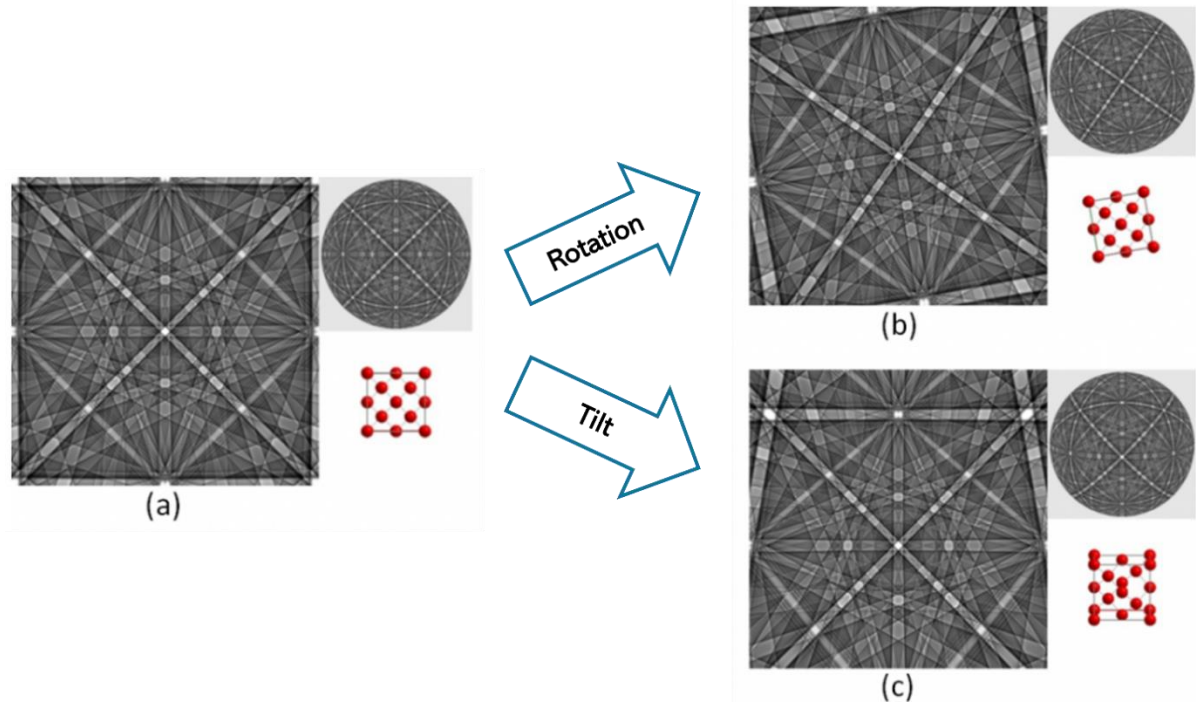


Figure 2.18. (a) Kikuchi bands corresponding to Si(100). (b) Variation in band appearance upon rotating the structure by 10° and (c) tilting the structure by 10° . The arranged red spheres represent the unit cell and its altered orientation due to rotation and tilt. (Source: <https://ssd.phys.strath.ac.uk/techniques/scanning-electron-microscopy/electron-backscatter-diffraction-ebsd/>)

This technique offers the capability to quantify the crystal structures present within a sample, discerning their orientation, sizes, and individual grain morphology [134]. Additionally, it enables the detection of strain distribution across epitaxial surfaces arising from disparities in lattice parameters [135]. In brief, strain mapping is achieved by scanning across a surface and analyzing the resulting Kikuchi bands. These bands are processed to obtain the KAM through post-processing calculations. This analysis quantifies the local misorientation across the surface under investigation, providing a measure directly correlated with local plastic deformation. By comparing this data with SEM images, such as those obtained through ECCI, it is possible to visualize misorientation associated with specific features, such as TDs. Figure 2.19 illustrates this concept, showing green areas that correspond to regions of higher misorientation due to the presence of TDs.

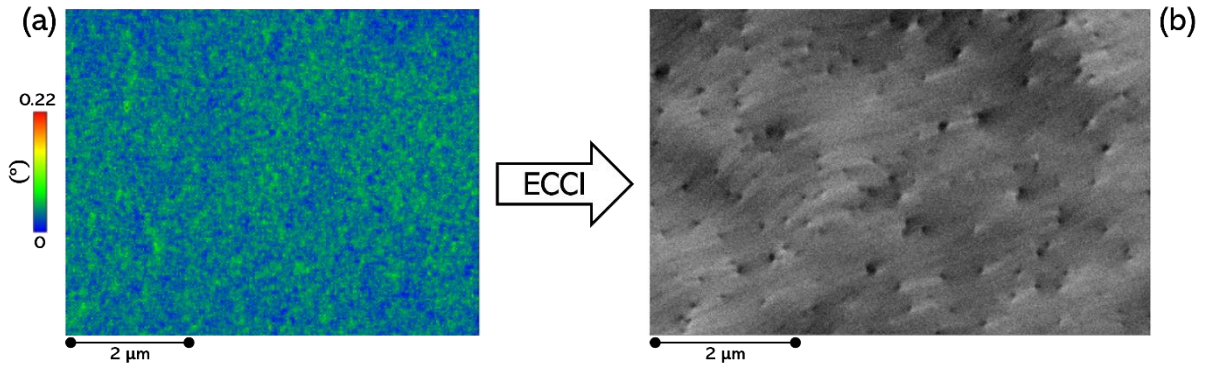


Figure 2.19. (a) KAM map of a GaN thin film displaying dislocations. (b) ECCI image illustrating individual dislocations from (a). (Source: <https://www.ebsd.com/ois-ebsd-system/dislocation-density-analysis>)

Building upon this foundation and acknowledging the substantial lattice mismatch between Ge and Si (as outlined in the introduction), research efforts have concentrated on ultra-thin Ge|Si virtual substrates, as will be elaborated in Section 3.2. These analyses seek to elucidate their impact on past and prospective solar devices, particularly in scenarios involving the integration of III-V materials within our MOVPE reactor setup. Like the AFM measurements, The EBSD measurements presented in this Thesis were conducted at *Universidad Carlos III (Leganés Campus)* using a High Resolution Scanning Electron Microscope (FESEM), specifically the FEI TENEO LoVac model.

2.3 Photovoltaic devices characterization

Once the layers are deposited on GON substrates, they underwent further processing to be converted into functioning solar cells. Briefly, the samples are carefully cleaved to prepare them for metallization. The metallization method used was gold evaporation. Initially, the front contact was deposited without issues following a photolithography process. However, the back contact presented a minor challenge: the position of the sample on the evaporator holder required that the part where the foil is suspended rest on the holder surface. To address this, a washer was used to apply pressure on the sample edge, minimizing potential damage by concentrating it on a less critical area. After metallization, the photolithography of the mesas is performed to allow for subsequent etching, which shapes the mesas into square-like devices with an area of 0.1 cm² each.

2.3.1 Quantum efficiency and reflectance

To measure quantum efficiency (the number of electrons produced per incident photon) and R , we utilized a custom-built setup (refer to the right panel of Figure 2.20). A Xenon lamp, providing a continuous spectrum in the visible range, serves as the light source. This light

passes through a Triax 180 monochromator, equipped with filters to remove harmonic wavelengths. The filtered light is then directed by a mirror towards a chopper rotating at a fixed frequency. The light beam is subsequently focused by a shutter to a spot size small enough to fit the surface of the device under test. The device is connected to the measurement system through two metallic contact tips (front and back) to complete the circuit. The detected signal is amplified and processed using the eLockIn method, which filters out ambient light based on the chopper frequency. Additionally, a monitoring cell is used to mitigate noise from the lamp, ensuring a high-quality signal for analysis. This configuration allows for the continuous recording and monitoring of the EQE using the software *Igor*, as shown on the left of Figure 2.20.

For reflectance measurements, the setup is modified slightly by positioning a small detector over the sample to capture the reflected light. The signal obtained is processed in the same manner, using amplifiers and other signal conditioning tools. Knowing R enables the calculation of the IQE using the following equation:

$$IQE(\lambda) = \frac{EQE(\lambda)}{1 - R(\lambda)} \quad Eq. 2.7$$

Beyond calculating IQE, EQE is crucial for determining the short-circuit current density (J_{sc}) under standard illumination conditions (1 sun). The equation for J_{sc} is given by:

$$J_{sc} = \frac{q}{hc} \int_{\lambda_2}^{\lambda_1} \Phi(\lambda) \cdot EQE(\lambda) \cdot d\lambda \quad Eq. 2.8$$

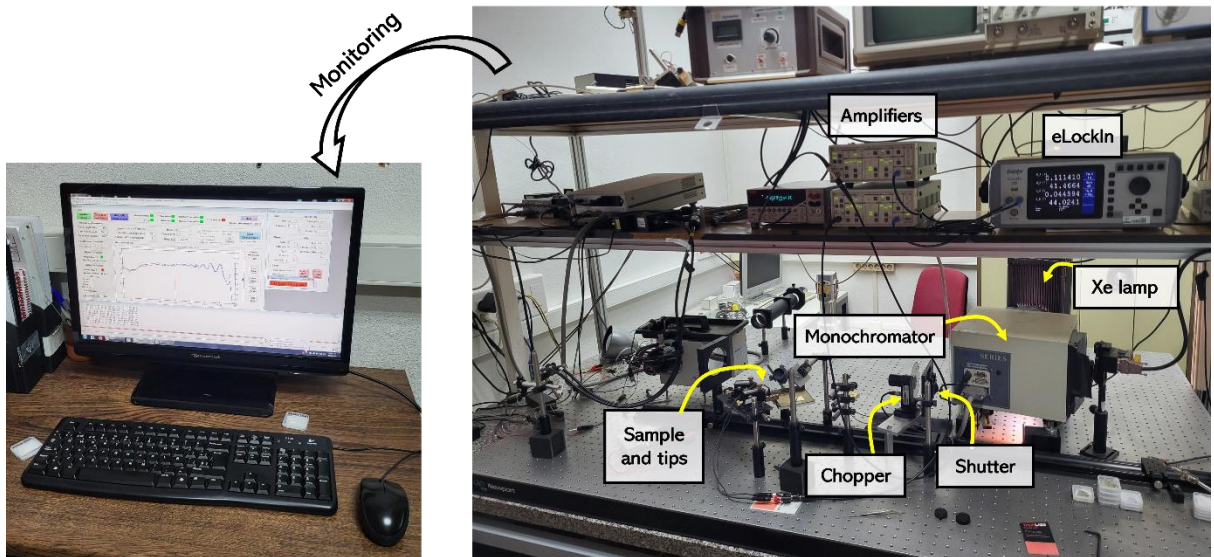


Figure 2.20. Custom-built setup for measuring EQE and reflectance at IES-UPM.

For MJSC, it is often necessary to measure the active subcells individually because the subcell with the lowest J_{sc} limits the overall J_{sc} of the MJSC. To achieve this, lasers with wavelengths of 970 nm, 700 nm, and 500 nm are used to saturate the subcells not being measured. This selective saturation is accomplished by using two lasers to leave the target subcell unsaturated and thus measurable. For instance, in a TJSC, to measure the EQE of the top cell, lasers at 970 nm and 700 nm are used to saturate the middle and bottom cells. Once the subcell with the lowest J_{sc} is identified, accurate characterization using I-V curves (discussed in the subsequent section) under standard illumination conditions can be performed.

This experimental setup has been effectively utilized in prior research conducted at IES-UPM [136], [137], as well as with the Ge|Si virtual substrate samples discussed in the introduction. In this Section 4.2 of this Thesis, EQE measurements were employed to evaluate the performance of the TJSC deposited on the GON substrates.

2.3.2 Current-Voltage curves

Obtaining the electrical behavior of a solar cell is one of the most common characterizations performed. I-V or J-V curves of a solar device illustrate the relationship between the current flowing through the device and the applied voltage across its terminals. This measurement is typically conducted by detecting the current while a range of voltages is applied. The setup available at IES-UPM is an in-house system comprising a Keysight B2902A source measure unit (SMU) that provides the voltage scan to the solar device through cables connected to two double contact tips, which serve as front and back contacts.

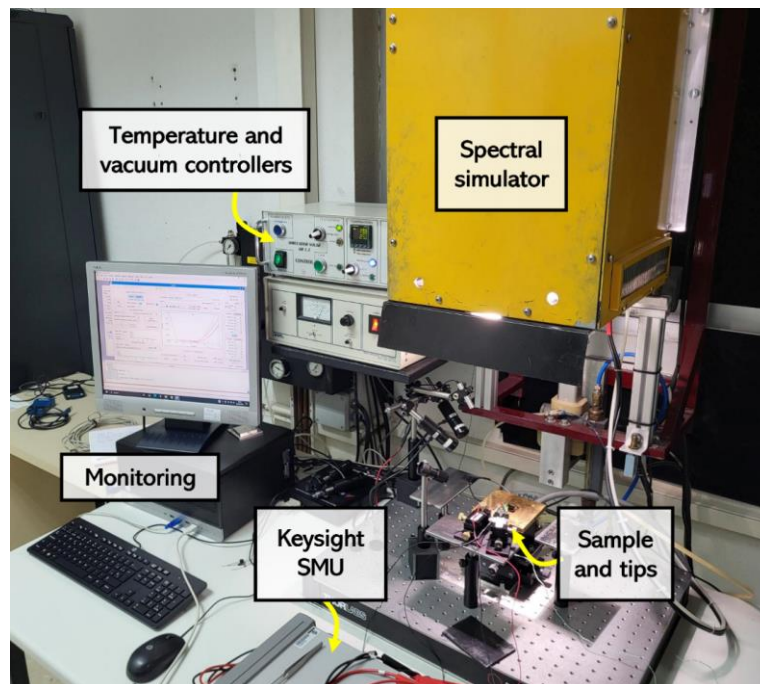


Figure 2.21. In-house setup for measuring dark and light I-V curves at IES-UPM.

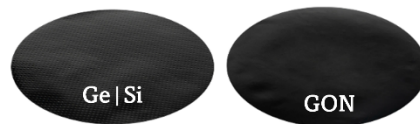
The sample is placed on a plate with a small hole and a vacuum system to hold the sample securely. This plate is equipped with a cooling system to maintain the sample at a constant temperature (usually around 25°C), counteracting the heating effect of the spectral simulator's light. The available spectral simulator, a Xenon arc lamp rated at 1000 W, provides an AM1.5G irradiance spectrum. The height of the spectral simulator can be adjusted to modify the power intensity as needed for specific samples during light I-V curve measurements. Additionally, the diode behavior can be assessed through dark I-V curves by switching off the spectral simulator. Measurements are recorded and monitored using the *Igor* software on a connected computer. A photograph of this setup is shown in Figure 2.21.

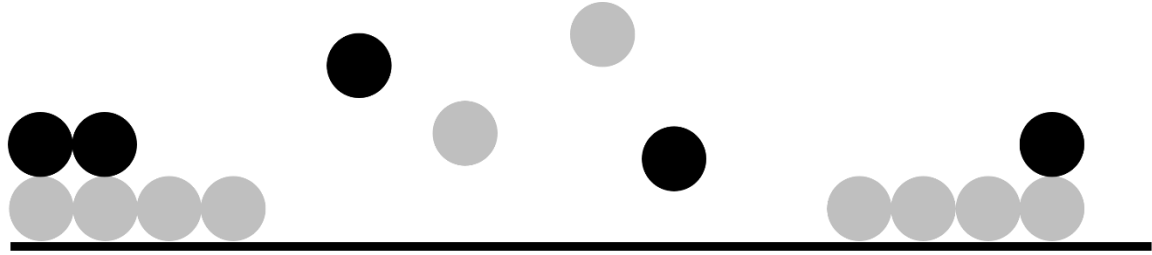
This experimental setup for both dark I-V curves [138] and light I-V curves [139] has been used in published reports, as well as with the Ge|Si virtual substrate samples discussed in the introduction. In Section 4.2, I-V measurements were employed to evaluate the performance of the TJSC deposited on the GON substrates.

In this chapter, a comprehensive analysis, discussion, and conclusion regarding the measurements of Ge|Si samples are presented. The structure of this chapter is organized as follows: initially, the presentation of the measurement data and images is divided according to different characteristic analyses, such as morphology, doping, and other relevant properties. Subsequently, the discussion and conclusions derived from these characterizations are detailed in a dedicated section.

Block I

Ge-based substrate analysis





Characterization of Ge | Si virtual substrates

CHAPTER 3

As detailed in the introductory chapter, the Ge|Si virtual substrates were manufactured at LPCIM-École Polytechnique (Paris) using RF-PECVD. For further details, the reader is directed to the relevant section of this chapter as well as the cited reference [75]. The provided samples have been categorized into two series: (1) an investigation into the impact of ultra-thin Ge layer thickness, and (2) an examination of the influence of deposition temperature on the ultra-thin Ge layer the with the same thickness. For convenience, these samples are systematically listed and designated in Table III.I and Table III.II, where the distinguishing parameters are clearly identified for ease of reference. Importantly, given that the critical thickness for dislocation formation of Ge on Si is less than 10 nm [140], the presence of certain defects and inhomogeneities within the Ge layer is anticipated. It is worth clarifying that this chapter will first present the results obtained from the characterization of these virtual substrates, followed by a section dedicated to discussing the information extracted from these measurements.

Sample	In-situ plasma clean	Thickness (nm)	Temperature (°C)
t20	Ar + H ₂	20	175
t40	Ar + H ₂	40	175
t60	Ar + H ₂	60	175
t120	Ar + H ₂	120	175

Table III.I. Growth parameters for the batch of different ultra-thin Ge thickness.

Sample	In-situ plasma clean	Thickness (nm)	Temperature (°C)
T175	SiF ₄ + H ₂	40	175
T200	SiF ₄ + H ₂	40	200
T225	SiF ₄ + H ₂	40	225
T250	SiF ₄ + H ₂	40	250

Table III.II. Growth parameters for the batch of different temperatures.

Aside from tabulated parameters, all samples were synthesized under identical conditions: a GeH₄ flow rate of 10 sccm, an H₂ flow rate of 500 sccm, a pressure of 1.7 mbar and a growth rate of 0.01 nm/s. The Si(100) substrates used had a diameter of 4 inches and a thickness of 525 μ m, with p-type (boron) doping and a resistivity of 1-10 Ohm-cm. The miscut for all Si substrates is 5° towards (111). To ensure consistency and comparability, the in-situ plasma cleaning process was maintained across the batches. Additionally, the radio frequency power applied was set at 10 W for all samples.

For clarity and simplicity in tables, samples were labeled based on their thickness and growth temperature. Thickness variations were denoted with a lowercase t followed by the thickness value in nanometers (e.g., t_{60} for a 60 nm thick sample). Similarly, samples grown at different temperatures were indicated with an uppercase T followed by the temperature in Celsius degrees (e.g., T_{200} for a sample grown at 200 °C). Henceforth, the former series shall be denoted as t -batch, while the latter series shall be designated as T -batch. Furthermore, some samples were subjected to additional GaAs and Ga(In)As deposition; the specific parameters consisting of a 50 nm GaAs nucleation layer followed by a 350 nm Ga(In)As contact layer, integral to an SJSC structure. Deposition occurred at 640 °C using high-purity AsH₃, TMGa, TMIIn for III-V epitaxies, and DTBSi and DETe for doping. The nucleation layers were doped with Si ($\sim 5 \cdot 10^{18} \text{ cm}^{-3}$) and the contact layers with Te ($\sim 3 \cdot 10^{19} \text{ cm}^{-3}$). During nucleation layer growth, molar flow rates were $4.4 \cdot 10^{-5} \text{ mol/min}$ for TMGa, $2 \cdot 10^{-2} \text{ mol/min}$ for AsH₃, and $1.69 \cdot 10^{-6} \text{ mol/min}$ for DTBSi. For the Ga(In)As layer, with $\sim 1\%$ indium content, flow rates were $4.46 \cdot 10^{-3} \text{ mol/min}$ for AsH₃, $1.75 \cdot 10^{-4} \text{ mol/min}$ for TMGa, $1.79 \cdot 10^{-6} \text{ mol/min}$ for TMIIn, and $7.31 \cdot 10^{-8} \text{ mol/min}$ for DETe. Nominal growth rates were 0.75 $\mu\text{m/h}$ for nucleation layers and 3.5 $\mu\text{m/h}$ for contact layers. To prevent arsenic desorption during cooling, AsH₃ flow was maintained at $2.2 \cdot 10^{-3} \text{ mol/min}$ until the temperature decreased to 300 °C. Subsequently, some of the III-V epitaxial layers were etched using a mixture of H₃PO₄ and HNO₃ in a 3:1 ratio to prepare the Ge surface for measurement. This acid mixture is highly selective [115], ensuring that modifications to the Ge surface are minimal and negligible for the purposes of our study.

3.1 In-situ measurements during the MOVPE growth process

As outlined in the methodology section 2.1.2, in-situ measurements using the RAS method are employed to evaluate the quality of the ongoing surface during the process. This MOVPE process begins with increasing the temperature to remove the protective oxide layer and any potential contaminants on the Ge wafer surface. Despite this bake at 640 °C, atoms from the reactor walls may still adsorb onto the Ge surface. It is believed that this effect is consistent across all samples, considering that the reactor walls were uniformly coated with GaAs. It is important to note that RAS detects the anisotropy of the surface. However, oxides and contaminants follow a random arrangement that does not favor any preferential direction of polarized light, resulting in no detectable signal during this stage. Subsequently, a pre-exposure flow of AsH₃ is introduced into the reactor for a duration of 20 seconds. Due to the high temperatures, AsH₃ decomposes, and As is deposited in its dimer form to stabilize the surface, ensuring high-quality epitaxial growth of III-V compounds. Following this stabilization,

the deposition of GaAs and Ga(In)As layers begins, as described in the introduction of Section 3. Further details of this process are provided in Section 4.4.

3.1.1 Pre-deposition analysis

Both t-batch and T-batch were compared with a reference of the same process conducted on a Ge standard wafer (reference sample). Figure 3.1 illustrates the RAS signal during the baking process at 640 °C. Overall, all samples exhibit virtually identical signals within the same batch, with the exception of t20 as shown in Figure 3.1(a). There is a noticeable protruding signal in this sample around the 3 eV range of the incident light (purple arrow in Figure 3.1(a)). This anomaly can be attributed to uncontrollable fluctuations in surface roughness, as the adsorbate levels are consistent across all samples. Furthermore, the possibility of oxides contributing to this anomaly is ruled out, given that the signal recorded during the oxide removal step (not shown) confirms their effective elimination. Finally, the reference sample exhibits a higher signal intensity in both instances, which is consistent with the expected outcome of a superior surface quality.

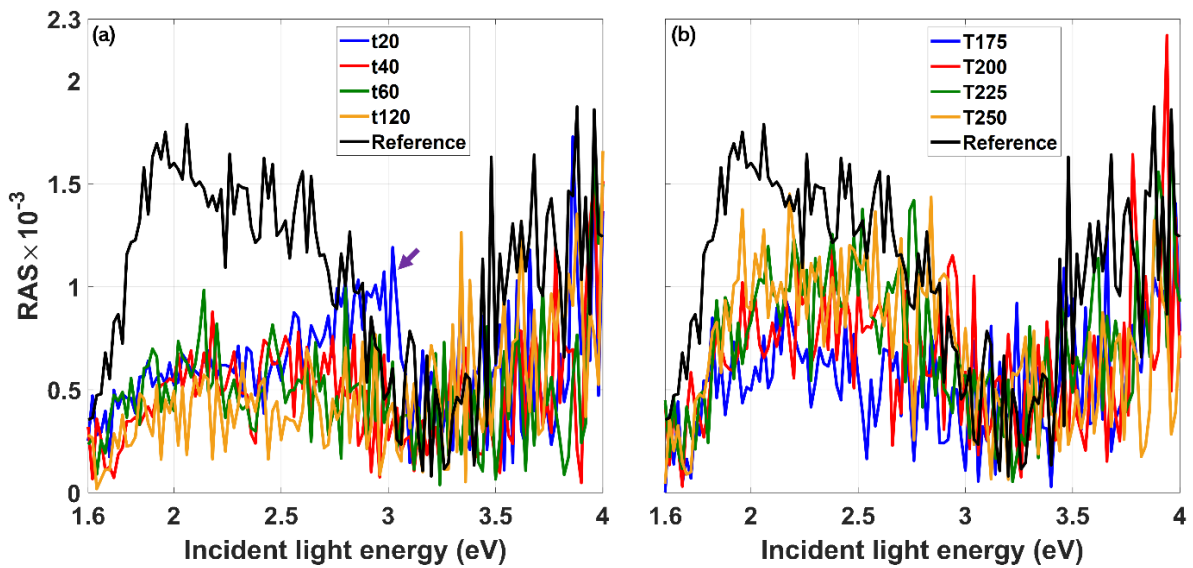


Figure 3.1. RAS spectra for both t-batch (a) and T-batch (b) during baking at 640°C. The purple arrow highlights the protruding signal around 3 eV.

Figure 3.2 presents a graphical representation of the DC signal obtained during the baking process. Spectroscopic analysis reveals different reflectance spectra in t-batch samples with varying intensity levels, whereas the overall shape remains consistent. Notably, the T-batch samples exhibit virtually identical DC signals, suggesting that the observed discrepancies in Figure 3.2(a) are primarily attributable to potential interactions between Ge thickness (associated with Fabry-Pérot oscillations) and surface roughness. The reference sample displays a higher signal intensity, likely due to reduced light scattering during measurement.

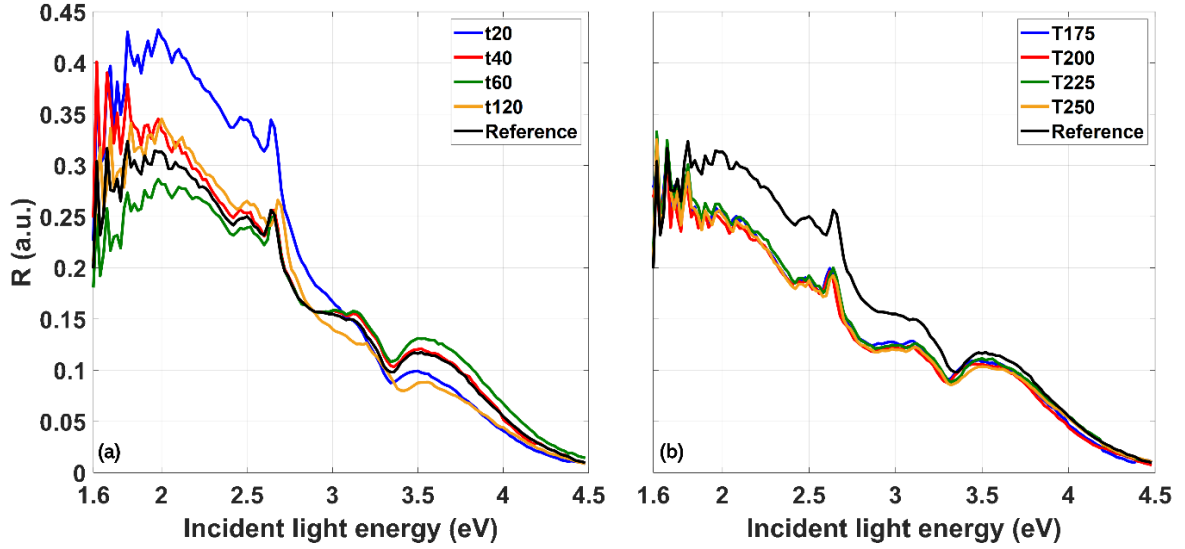


Figure 3.2. Reflectance spectra for t-batch (a) and T-batch (b) during baking at 640°C.

3.1.2 Ongoing III-V deposition assessment

All previous analyses focused on the Ge surfaces. The characterization of the III-V depositions on Ge follows the methodology outlined in reference [88], where the surface reconstruction (1×2) or (2×1) due to released precursors is crucial. Specifically, the initial peak corresponding to the GaAs nucleation layer exhibits a slight attenuation, as indicated by the left dashed line in Figure 3.3. This suggests a surface reconstruction effect induced by precursor placement on the Ge surface. This peak is expected to display a reduced intensity relative to the second peak, which is a characteristic of the same nucleation process. The presence and disposition of these peaks, when aligned with reference peaks, indicate a high-quality III-V epitaxy. Deviations from the expected peak configuration may not ensure the same surface quality or surface reconstructions.

Figure 3.3 illustrates the transient mode during this stage for both sample batches. Figure 3.3(a) displays the RAS signal in transient mode, measured at 2.1 eV, for the t-batch. For all samples in this batch, the peak intensities do not align with the expected reference values. Consequently, it is anticipated that the morphological quality of the GaAs nucleation layer, and subsequently the Ga(In)As layer, may be suboptimal. A notable exception could be the t120 sample, as it follows the expected trend marked by the reference sample, although presenting, different intensities. This discrepancy might suggest a slightly similar morphology or surface reconstruction when comparing the t120 and reference sample. The signal intensity of the Ga(In)As deposition, denoted by a dashed line on the right, exhibits a lower amplitude compared to the reference samples. Furthermore, the observed peak shift in earlier times is attributed to a change in the GR of the samples, which will be elucidated in further detail. For the T-batch (Figure 3.3(b)), the RAS signals exhibit a similar shape across all samples within

the batch, as seen in previous figures. Nonetheless, the peak intensities differ from those of the reference samples, indicating a likely poorer morphology. Despite this, the consistency in peak shape within the batch suggests that the surface morphologies, although inferior, are at least comparable to each other. The analogous inference drawn from the t-batch analysis can be extrapolated to the Ga(In)As deposition layer, wherein the observed peaks exhibit a temporal displacement towards earlier times.

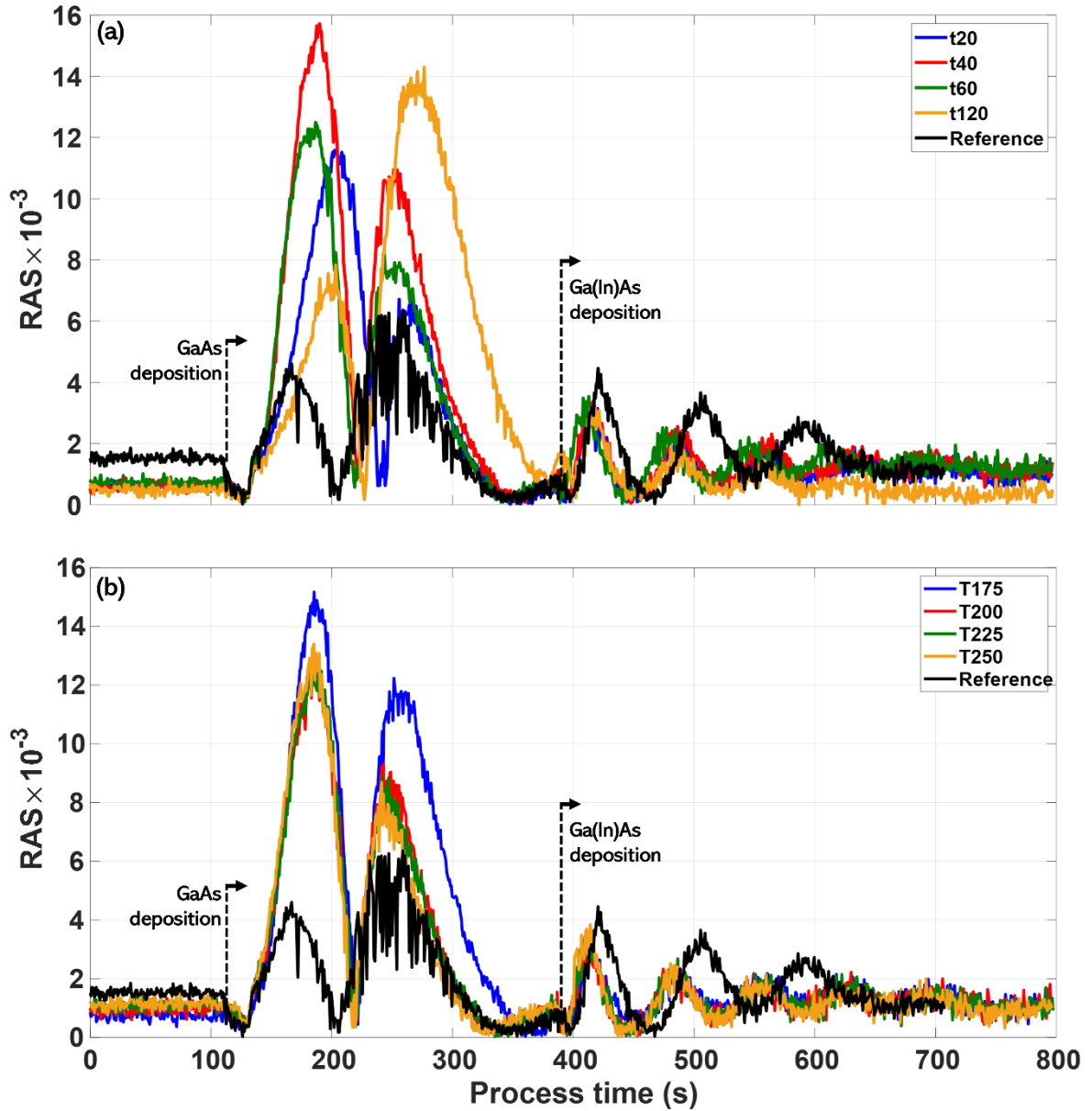


Figure 3.3. RAS signal (transient mode measured at 2.1 eV) for both t-batch (a) and T-batch (b) samples during III-V deposition. The black dashed lines indicate the initiation of each stage of the epitaxy process.

The surface roughness can modulate the GR by influencing various factors, including surface energy, which enables the trapping of adatoms in local minima, thereby reducing their mobility and potentially slowing down the growth process. Additionally, shadowing effects, where taller features impede the deposition of material on lower regions [141], can result in non-uniform GRs across the surface. Furthermore, the presence of defects, such as dislocations, can exacerbate surface roughness, leading to increased nucleation rates and potentially accelerated initial growth rates due to the preferential attachment of adatoms to step edges and kinks [142]. Figure 3.4 depicts the DC signal in transient mode, measured at 2.1 eV, observed during the growth process. The t-batch samples exhibit varying signal amplitudes attributable to different Ge thicknesses and expected irregularities. Despite the similar starting point for the reference sample and all depositions (left vertical black dashed line), a slight acceleration in GR is discernible on the Ge|Si virtual substrates (thick black arrow), particularly evident in Ga(In)As deposition process (right vertical black dashed line). This observation aligns with the peak shifts described and illustrated in Figure 3.3(a). This same trend is consistently observed during nucleation, except for t20 in the nucleation stage, and may be partly attributed to the underlying roughness of the samples. The definitive conclusion is complicated by several factors. In addition to the potential causes discussed at the beginning of this paragraph, the reference sample has a 6° miscut towards (111), unlike the Ge|Si samples, which have a 5° miscut towards (111). There is no clear explanation of how this miscut difference affects the GR. Further studies on the effect of Fabry-Pérot oscillations due to the standard Ge (150 μm) and the nm-range Ge on thick Si are necessary to clarify this issue. Despite concerns about surface quality, the DC signal remains consistent and follows a straight line, as represented by the horizontal black dotted line. This stability indicates that there is no significant drop in signal intensity, suggesting that the surface roughness does not have a severely detrimental effect.

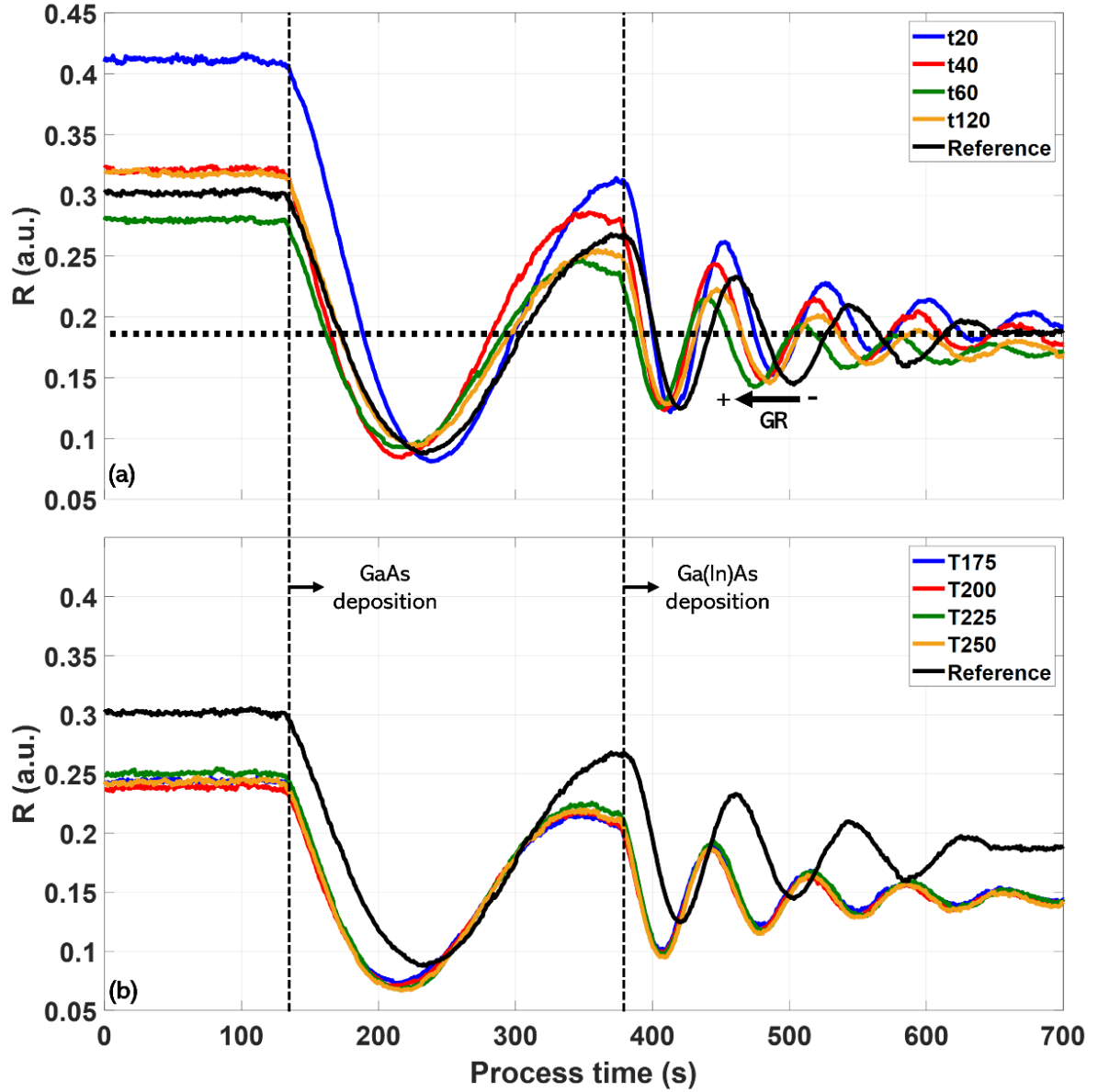


Figure 3.4. Reflectance signal (transient mode measured at 2.1 eV) for t-batch (a) and T-batch (b) during III-V deposition. Vertical dashed lines denote the start of each epitaxy stage. The thick black arrow indicates the correlation between valley positions and GR. The horizontal dotted line represents a linear signal evolution with no observed drop-off.

3.2 Lattice deformation

Prior to any deposition processes, the significant lattice mismatch between the deposited Ge and the Si substrate was analyzed using the EBSD method, with results represented in a KAM map. These measurements were conducted at *Universidad Carlos III de Madrid* by Elisa García-Tabarés. The basic concepts of this method were introduced in section 2.2.6.2 for initial comprehension. The Ge|Si samples underwent III-V epitaxial growth followed by the corresponding etching process, as detailed in the latter texts of section 3.

Figure 3.5 presents the KAM maps for the t-batch samples. It is suspected that the points of maximum deformation may coincide with the red points. However, these red points are not indexed, and we cannot accurately determine their exact value. The EBSD analysis reveals an inhomogeneous distribution of misorientation/strain across the Ge surface. Specifically, the t40 and t60 samples exhibit "clusters" of misorientation in a non-patterned manner. Additionally, there is a slight increase in misorientation with increasing Ge thickness, as indicated by the progressively and slightly brighter green regions in the images. This trend culminates in the t120 sample, which shows a marked increase in green brightness, indicative of a high level of plastic deformation and a lack of reproducibility, as evidenced by the two very different outcomes within the same sample.

Several images in Figure 3.5 reveal subtle straight lines in areas of high deformation. In sample t20, these lines are more discernible due to reduced deformation, with the angle between the intersecting lines approximating 50° . Despite the substantial lattice mismatch that predicts cracks along the $\langle 110 \rangle$ direction [64], the observed cracks do not consistently form the expected 90° angle relative to the $\langle 110 \rangle$ directions. This deviation indicates that additional experiments are required to verify this observation, as a larger number of EBSD measurements are needed. At present, this observation cannot be definitively attributed to any specific cause and remains classified as a discrepancy.

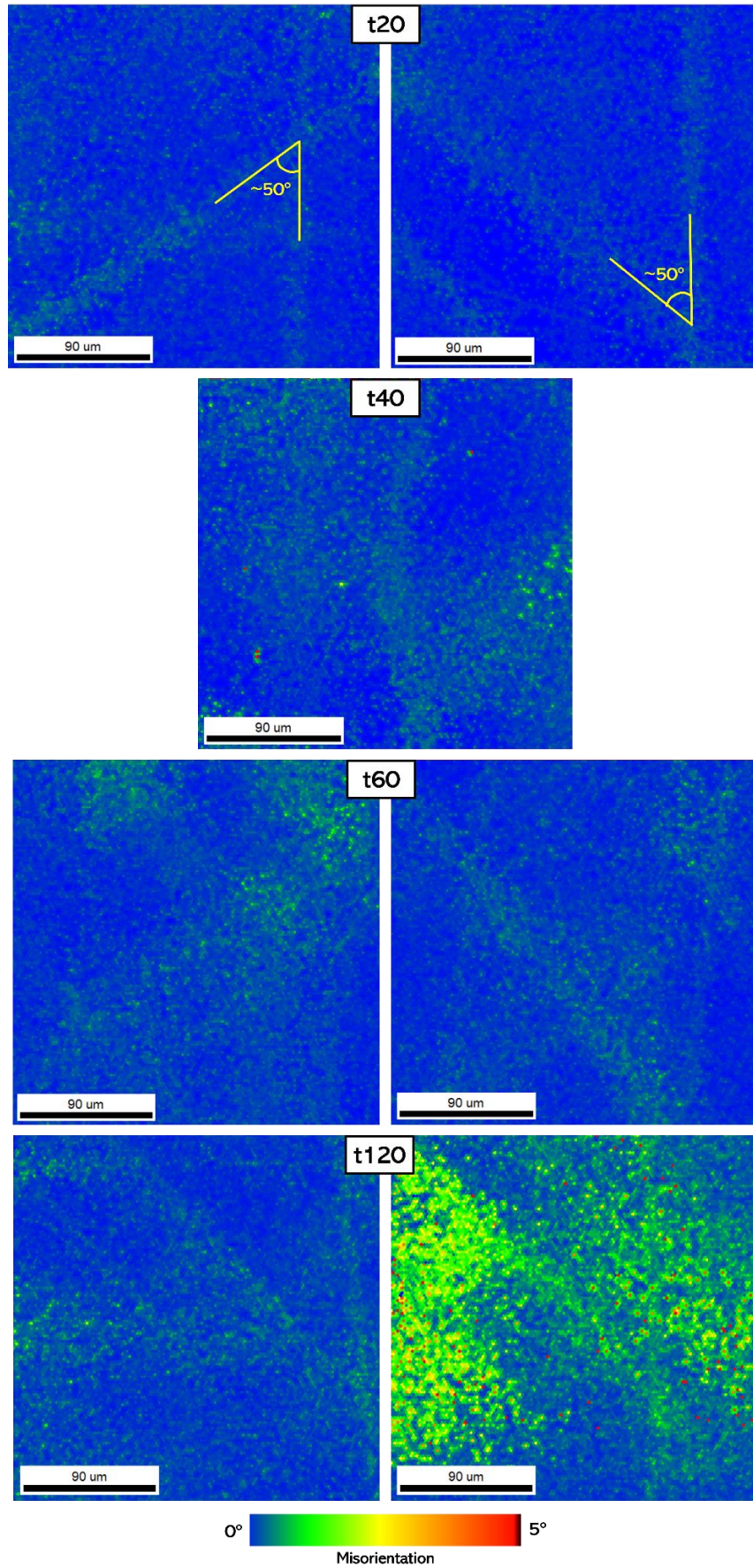


Figure 3.5. KAM maps for the *t*-batch samples.

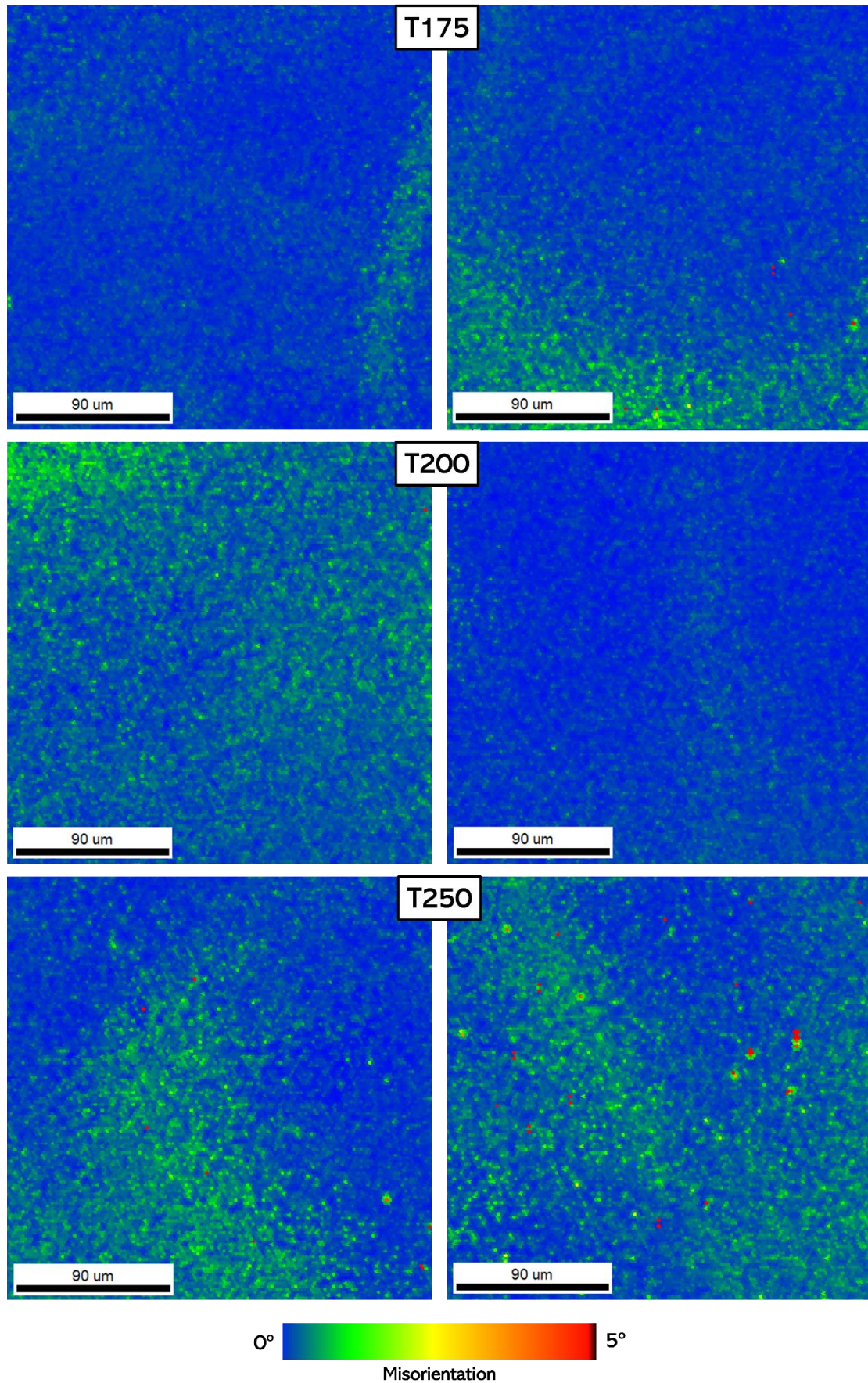


Figure 3.6. KAM maps for the T-batch samples.

For the T-batch samples (Figure 3.6), the analysis yields comparable observations. Again, as in the previous figure, we encounter the same issue where the red points are not indexed. The "cluster"-like misorientation distribution is less prominent, suggesting a slightly more uniform distribution overall. In the case of T250, this uniformity appears more pronounced, although it is not absolute. The issue of reproducibility remains, as evidenced by the differences in the two images of the same samples (T175 and T200). While significant plastic deformation is present, it is less severe than in t120. Notably, no surface cracks were apparently detected in these samples.

As mentioned earlier in this chapter, the Ge|Si samples were subjected to GaAs epitaxy at high temperatures, raising concerns about potential substrate degradation. To investigate this, an identical RF-PECVD process for Ge deposition was performed on standard Ge wafers (Ge/Ge) with a 6° miscut towards (111). Subsequent EBSD analysis was conducted without any further deposition on these wafers. Figure 3.7, despite a reduction in plastic deformation, displays some residual deformation persists, and the misorientation distribution remains heterogeneous.

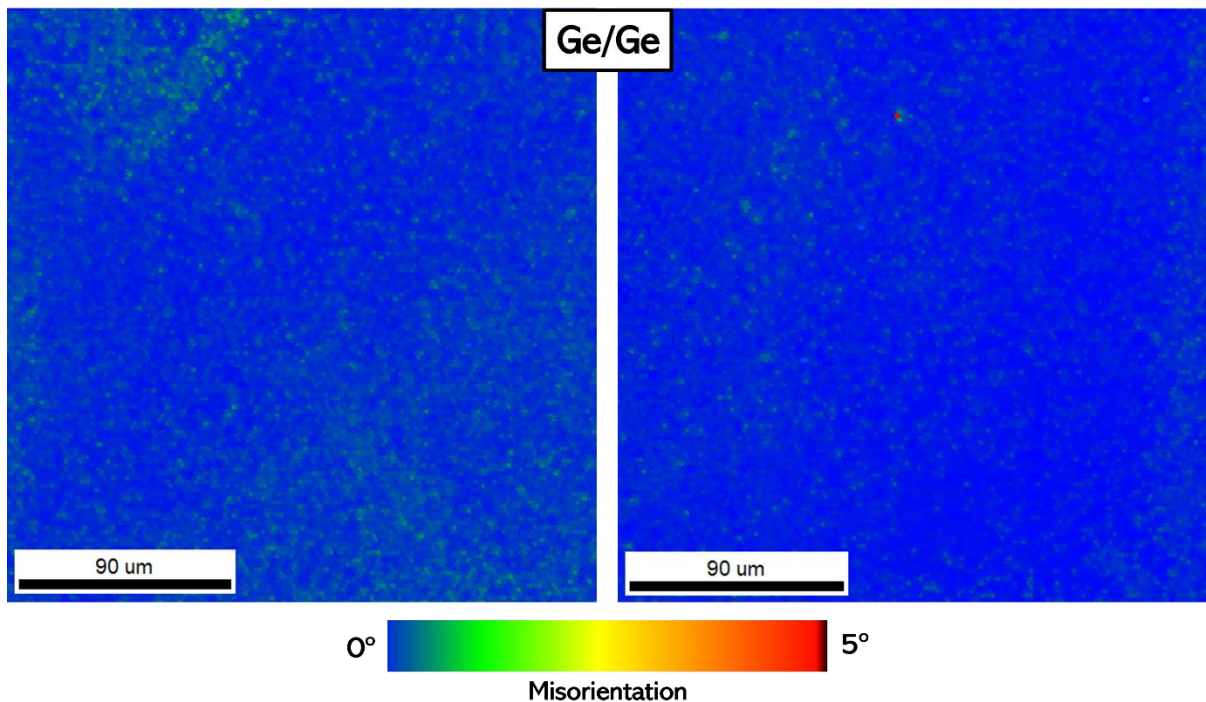


Figure 3.7. KAM maps for the sample with deposited Ge on standard Ge substrate (Ge/Ge).

3.3 Interface analysis

This section examines the morphological characteristics of Ge|Si interfaces, with a subsequent evaluation of Ge/Ge interfaces for direct comparison. Figure 3.8 presents ADF-STEM images of samples t40 and t120. The t40 sample exhibits a brighter contrast across the entire layer

compared to t120, indicating variations in defect types or their distribution. Moreover, t40 also contains defect-free regions (yellow rectangles) within its transverse layer, a feature not observed in t120. Magnified views of t40 confirm these defect-free zones. Additionally, misfit dislocations are prominently present at both interfaces (yellow ellipse). The linear misfit dislocation density is calculated to be $9.8 \cdot 10^5 \text{ cm}^{-1}$ for t40 and $1.1 \cdot 10^6 \text{ cm}^{-1}$ for t120, suggesting that the lower density in t40 (around 11% lower) may account for the presence of defect-free areas. BF-TEM images of the magnified region of t40 provide clearer evidence of strain relaxation. The inset of the figure reveals instances where certain dislocations emerge at the Ge|Si interface (red arrow). Additionally, in most cases, these dislocations propagate entirely through the layer, extending up to the surface (blue arrows), thereby corroborating the presence of deformation and surface defects depicted in Figures 3.5 and 3.6.

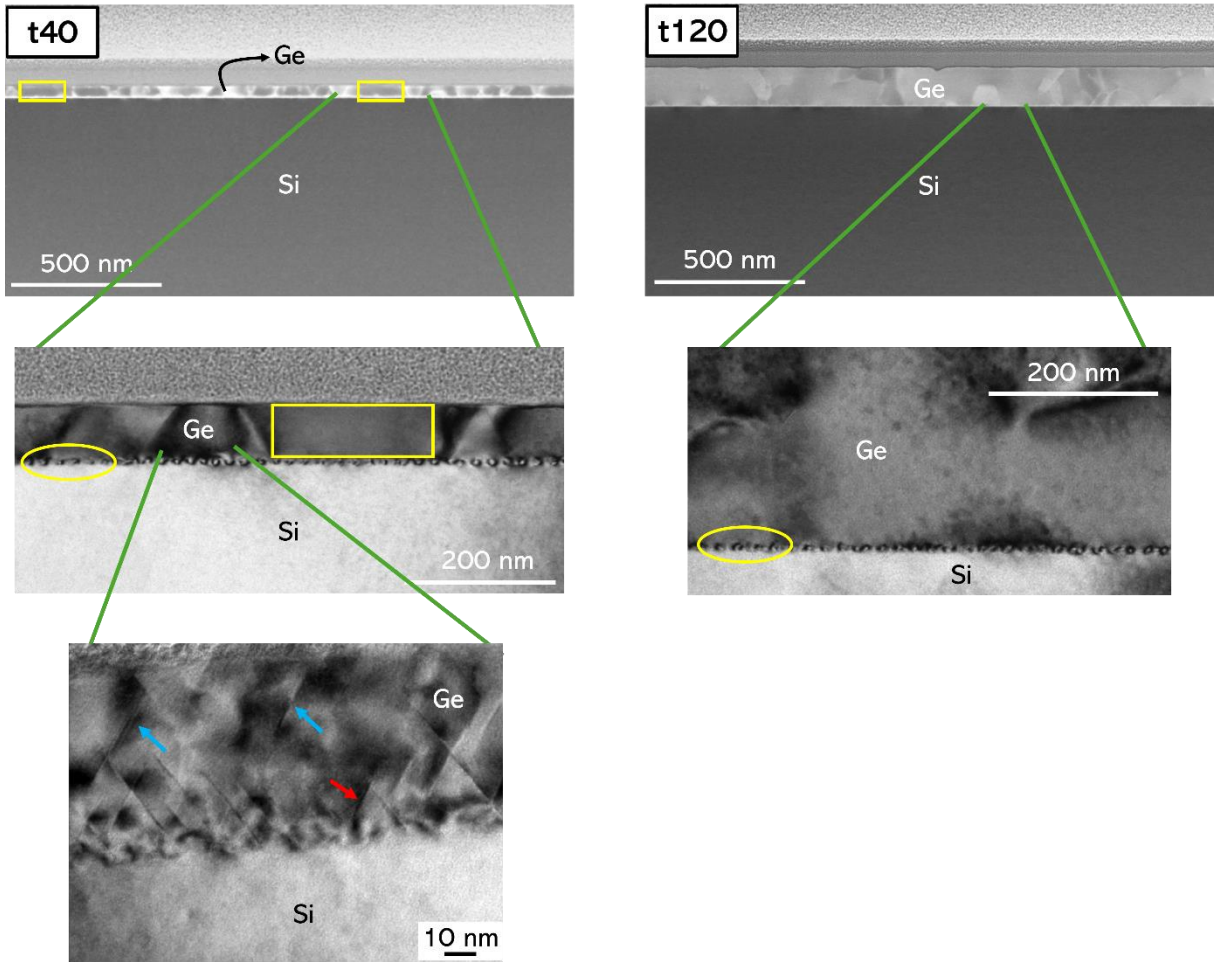


Figure 3.8. The first row presents ADF-STEM images of samples t40 and t120, while the subsequent images are obtained via BF-TEM method. Yellow rectangles highlight defect-free regions, and yellow ellipses indicate misfit dislocations at the Ge|Si interface. Blue arrows denote cracks reaching the Ge surface, and the red arrow indicates self-annihilated cracks.

The misfit dislocations observed are further illustrated in Figure 3.9, where HRTEM images provide a closer inspection of the interfaces for t40 and t120 samples. Both samples display typical misfit dislocation structures, with discontinuities in Si columns within the Ge layer (blue and green lines). These dislocations exhibit the characteristic 60° orientation in Ge on Si (pink arrows) in both possible orientations [143]. The spacing between misfit dislocations ranges from 4 to 5 nm, consistent with the spacing observed in low-temperature Ge deposition on Si [144].

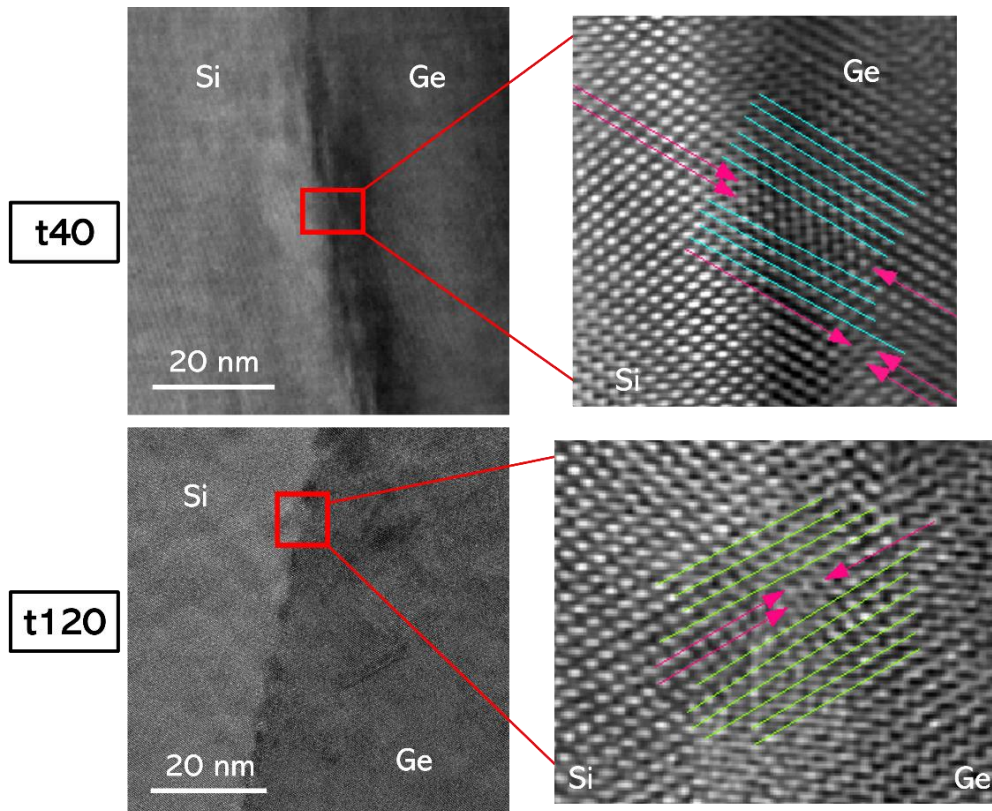


Figure 3.9. HRTEM images of the Ge/Si interface illustrating the dislocations disrupting the atomic arrangement continuity (blue and green lines) due to significant lattice mismatch. Pink arrows indicate the characteristic 60° orientation of dislocations in Ge on Si, showing both possible orientations.

For the comparative analysis of Ge/Ge samples, ABF-STEM imaging was conducted, as illustrated in Figure 3.10. In Figure 3.6(a), the different Ge layers are discernible due to the presence of a clear interface. Additionally, defects are minimal, although some defects can be observed extending from the interface to the surface (yellow arrows). A higher magnification ABF-STEM image from another region of the sample (Figure 3.6(b)) reveals these defects near the interface, but not extending to the surface (red arrows). Defects indicated by yellow arrows confirm the minor plastic deformation observed in Figure 3.7.

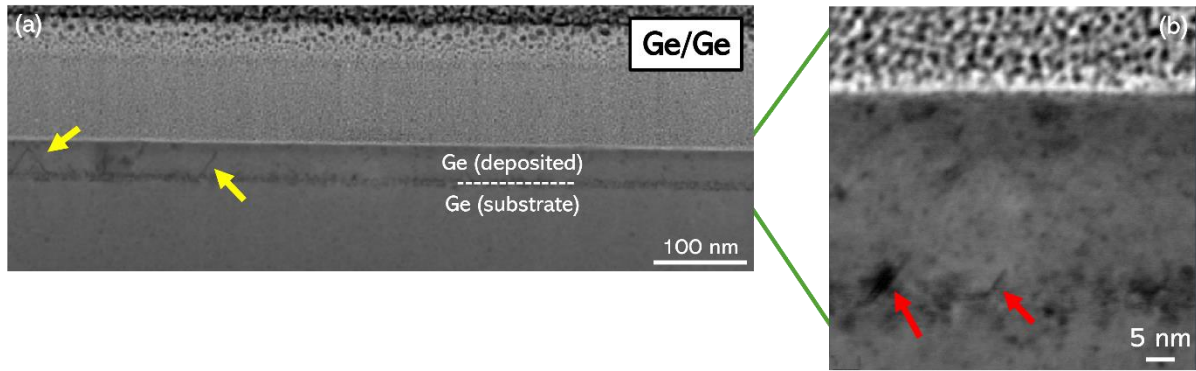


Figure 3.10. ABF-STEM micrographs of Ge layers deposited on Ge substrates (Ge/Ge). (a) Yellow arrows highlight cracks extending from the Ge/Ge interface to the surface. (b) Magnified view of a region where sessile cracks are observed near the Ge/Ge interface, not extending to the surface.

3.3.1 Effect of MOVPE thermal load on Ge surface

Figure 3.11 presents both AFM and TEM images of two types of samples corresponding to t40: one with III-V deposition (Figure 3.11(a)) and one without epitaxially deposited layers (Figure 3.11(b)). For the remainder of this section, the sample with the epitaxial layers will be referred to as the Epi-Sample, and the sample without the epitaxial layer will be referred to as the Raw-Sample. It was observed that the roughness of the Ge surface decreased slightly after the epitaxial process. AFM measurements indicate that the RMS roughness values are 0.564 nm for the Raw-Sample and 0.35 nm for the Epi-Sample. For further details on the epitaxial process and the subsequent etching applied to the Epi-Sample to expose the Ge surface, please refer to the introduction of Section 3.

One might question whether the observed effects are directly associated with the deposition of III-V materials. As will be detailed later, our working hypothesis posits that the surface smoothing of Ge is attributable to a reduction in surface energy induced by thermal load application during the MOVPE process. To explore this hypothesis, a new sample was prepared with a Ge layer thickness of 40 nm, deposited at a temperature of 200 °C. This sample underwent AFM analysis both before and after exposure to a thermal load under H₂ atmosphere. This treatment replicated the duration and temperature conditions detailed in section 3 but excluded the introduction of any precursors or metalorganics into the reactor. The AFM results are presented in Figure 3.12. As illustrated, the surface morphology evolution closely resembles that observed in Figure 3.11, with a high degree of similarity in the RMS roughness values. Thus, the thermal load effectively smooths the Ge surface, supporting the hypothesis that a reduction in surface energy occurs.

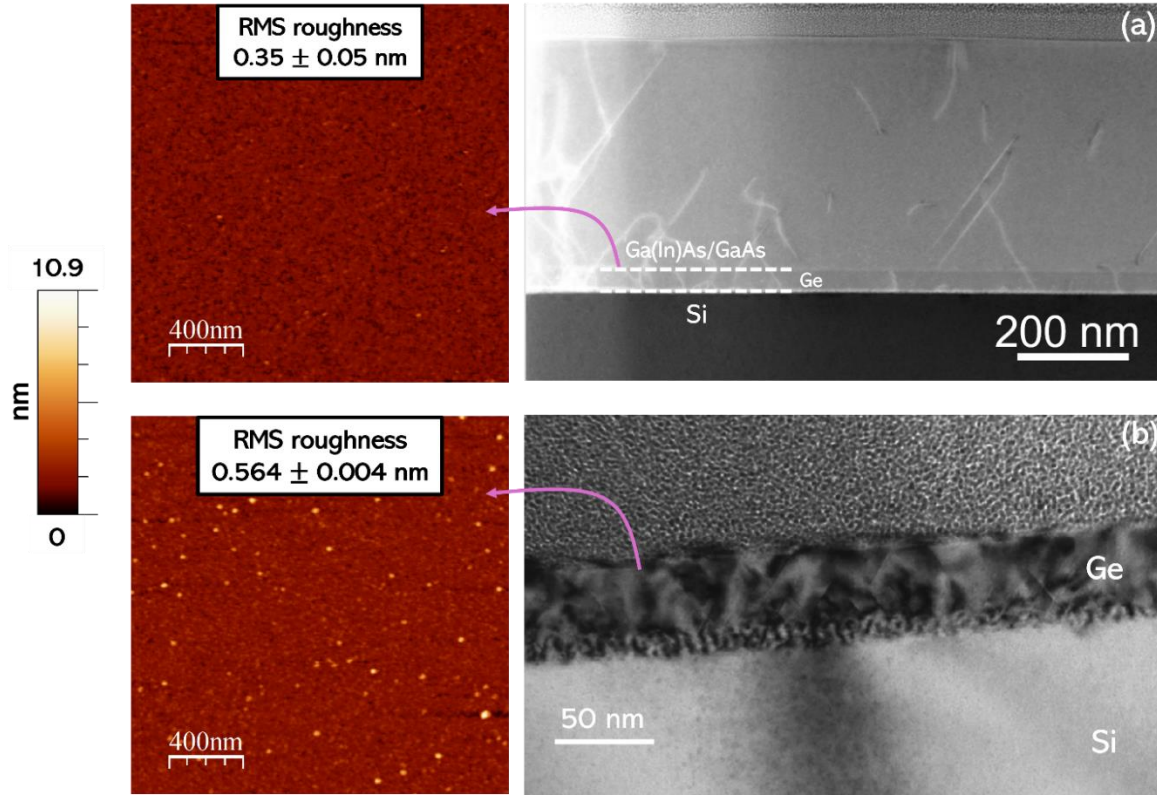


Figure 3.11. TEM micrographs (right) and corresponding representative AFM scans (left) for Epi-Sample (a) and Raw-Sample (b).

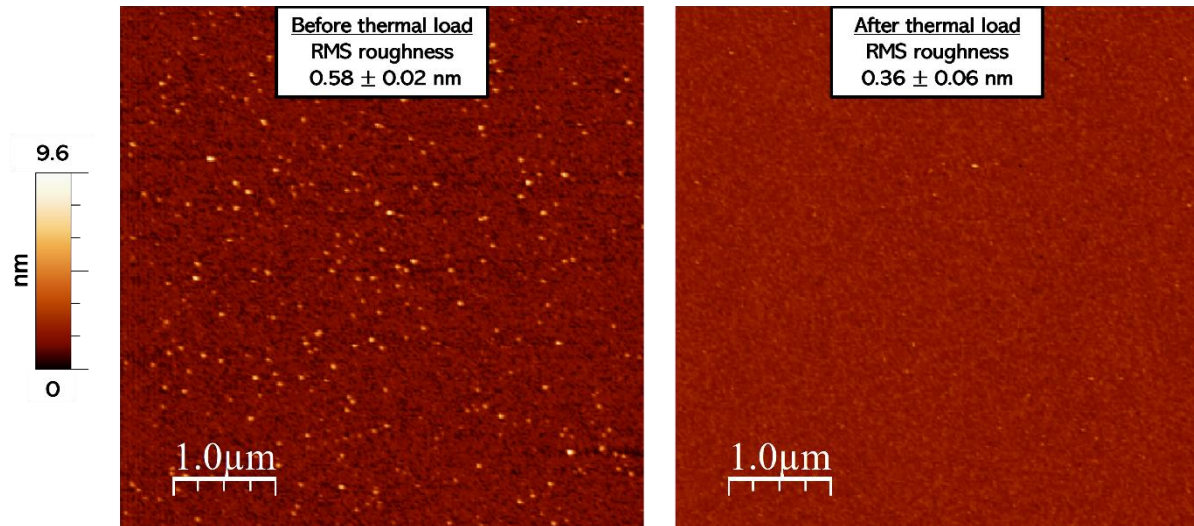


Figure 3.12. AFM images of Ge/Si samples before (left) and after (right) MOVPE thermal load.

3.4 Threading dislocations impact on III-V layers

Within this section, we undertake an examination of epitaxially deposited Ga(In)As/GaAs layers. The growth conditions are outlined in preceding texts within section 3, albeit excluding details pertaining to the etching process.

Figure 3.13 presents ADF-STEM images depicting the entire structure of Ga(In)As/GaAs/Ge|Si for t40 and t120. Visual differentiation between GaAs and Ga(In)As proves challenging due to the low In content ($\sim 1\%$), rendering these materials virtually indistinguishable. Evidently, numerous defects manifest within the Ge layers, propagating through the Ga(In)As/GaAs layer (green arrows). This occurrence is characteristic of materials with a high lattice mismatch, such as GaAs directly deposited on Si [145]. Sample t120 exhibits a higher TDD compared to t40. However, the TDD values across these samples demonstrate minimal disparity, remaining within the same order of magnitude, approximately $4 \cdot 10^9$ - $6 \cdot 10^9 \text{ cm}^{-2}$. Upon closer inspection of both interfaces (Ge|Si and GaAs/Ge), as GaAs and Ga(In)As are discernibly identical owing to the low indium content, observations from the t120 samples elucidate a different absence of misfit dislocations at the GaAs/Ge interface. In contrast, as previously illustrated in Figure 3.4, such dislocations are conspicuously present at the Ge|Si interface (yellow ellipse). Thus, it becomes evident that new misfit dislocations do not originate from the GaAs/Ge interface.

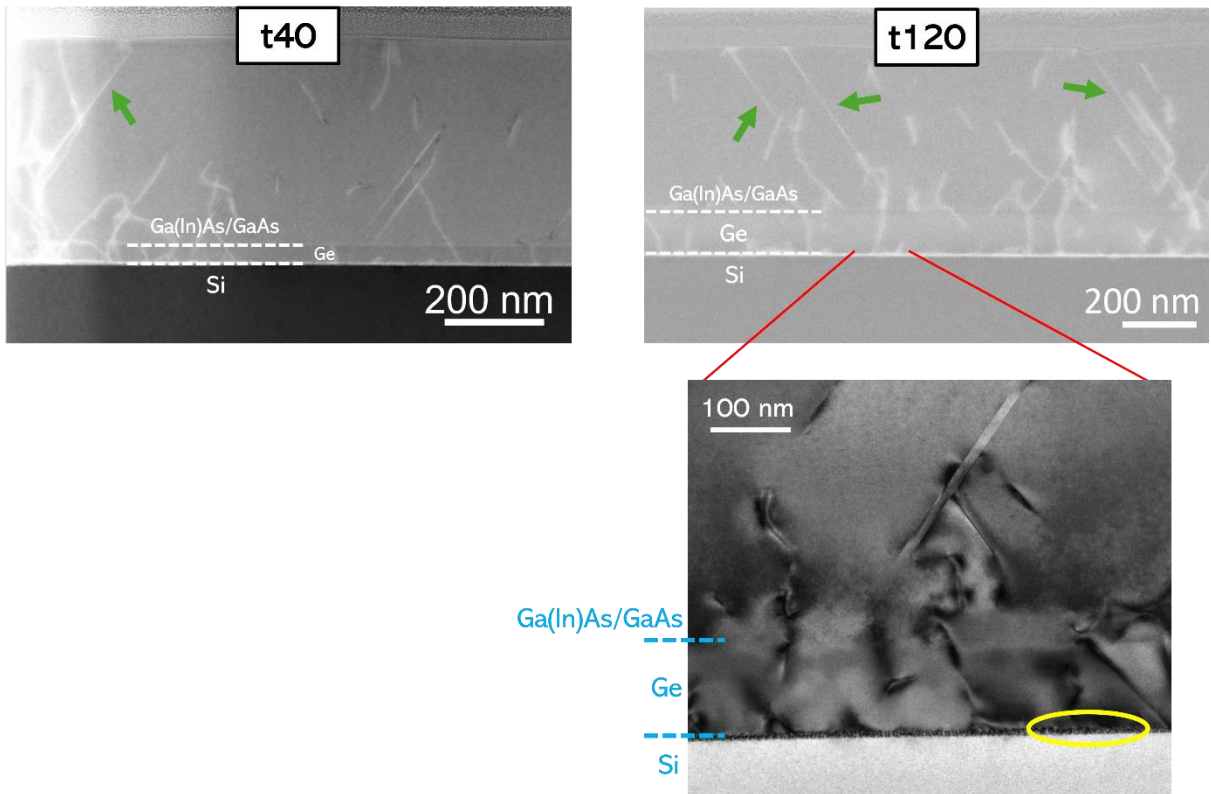


Figure 3.13. ADF-STEM images depicting the Ga(In)As/GaAs/Ge|Si structure for samples t40 and t120 (upper section) and a magnified ADF-TEM image for sample t120 (below section), illustrating the two interfaces. Green arrows indicate dislocations propagating from the Ge layer to the surface, while the yellow ellipse highlights misfit dislocations at the Ge|Si interface.

It has already been demonstrated that dislocations can propagate to the surface of the entire structure. However, the scope of TEM-based images is limited by its inherently small field of view. To overcome this limitation, ECCI (based on SEM microscopy) provides broader area

images of the Ga(In)As surface, which is the top layer of the structure. Figure 3.14 displays ECCI images at two different magnifications for the t-batch samples. In these images, each spot corresponds to a dislocation, with several examples highlighted by yellow arrows.

The visibility of these spots in ECCI images depends on the orientation of the dislocations relative to the atomic lattice (as discussed in the methodology chapter). Consequently, the observed spots may represent an inferior limit of the TDD because the dislocations traverse the (111) planes along four possible Burgers vectors [146]. To confirm this hypothesis, further characterization techniques should be employed, although this may not be necessary as will be discussed in the conclusion section. From these ECCI images, the TDD values for each sample were determined, along with their respective uncertainties, as shown in the Table III.III. In general, the TDD values obtained via ECCI are consistent with those obtained through TEM.

Sample	t20	t40	t60
TDD (10^9 cm^{-2})	4.6 ± 0.4	5.0 ± 0.5	5.0 ± 0.4

Table III.III. Values of TDD for the t-batch.

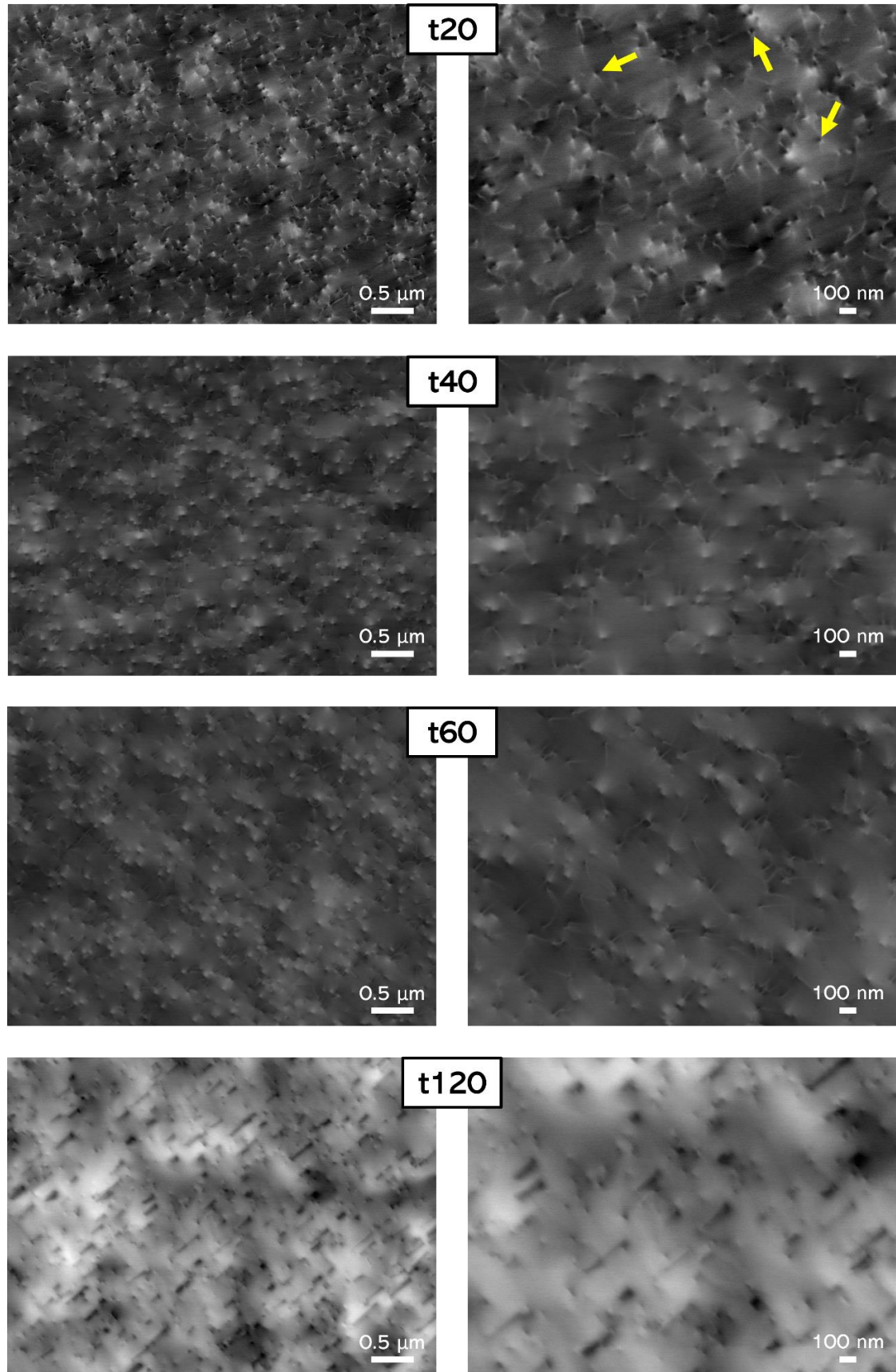


Figure 3.14. ECI images at two different magnifications for the *t*-batch samples, organized in columns. Yellow arrows indicate selected TDs for reference.

3.4.1 Study of Ga(In)As surface morphology

To this point, the primary focus has been on the in-depth study of interfaces and the brief assessment of defects in the deposited structure. However, understanding the surface morphology is crucial since rough interfaces can detrimentally impact the performance of certain devices [147]. Additionally, surface roughness impacts optical properties due to scattering effects, as supported by both theoretical [148] and experimental [149] reports. It also affects the quality of epitaxial growth, which is a concern if these structures are to be used in future MJSCs. Therefore, an examination of the Ga(In)As surface morphology is conducted through AFM scans. Although this analysis primarily targets the initial layer, it can provide insights applicable to possible subsequent epitaxial layers.

Figures 3.15 and 3.16 display representative $2 \times 2 \mu\text{m}^2$ AFM images of the t-batch and T-batch samples, respectively. All samples exhibit inhomogeneous surface morphology with RMS roughness values that do not follow a clear pattern and show high values for epitaxy purposes (see Table III.IV and Table III.V). This observation is noteworthy, as epi-ready Ge substrates exhibit RMS roughness values below 0.3 nm [58]. The values presented in Table III.IV and III.V are noticeably higher than those reported in [150], where GaAs surfaces on 200-300 nm of Ge on Si exhibited RMS roughness below 0.5 nm. Despite the similar substrate characteristics (5° miscut and Si(100) orientation), the GaAs layer thickness in that study was 1 μm , in contrast to approximately 400 nm (GaAs + Ga(In)As) in this work. This aligns with the established understanding that the GaAs surface becomes smoother as it undergoes epitaxial deposition [151], suggesting that additional GaAs deposition would further smooth the surface. However, this smoothing process begins with the initial roughness of the surface substrate. As illustrated in Figures 3.11 and 3.12, the initial RMS roughness is measured at 0.35 nm. In contrast, the RMS roughness of the Ga(In)As surface significantly increases, ranging from six times higher (under optimal conditions) to up to fourteen times higher (under suboptimal conditions). This observation supports the hypothesis that the strained surface (Figures 3.5 and 3.6) and the presence of dislocations (Figures 3.8 and 3.14) degrade the crystal quality of the deposited layer, which is also reflected in the variations of the RAS signal compared to the GaAs on Ge standard (section 3.1).

Sample	t20	t40	t120
RMS roughness (nm)	1.79 ± 0.10	1.75 ± 0.03	5 ± 1

Table III.IV. Values of RMS roughness for the t-batch.

Sample	T175	T200	T225	T250
RMS roughness (nm)	2.7 ± 0.4	1.7 ± 0.2	2.0 ± 0.1	1.6 ± 0.1

Table III.V. Values of RMS roughness for the T-batch.

The images display a cusp-like surface, characteristic of layers with high lattice mismatch, leading to compressively strain-induced modulations [152]. Furthermore, all samples feature a rooftop-like structure with a periodic separation, denoted as d . Literature attributes these lines to double-atom steps or the miscut in the substrate [153]. As noted in the introduction of Section 3, the Si substrate has a 5° miscut. Considering this angle and step heights of one or two atoms, d should be approximately 6 nm and 12 nm, respectively. However, the observed values primarily fall into two ranges: 20 to 60 nm and 110 to 150 nm. These values were calculated from several profiles obtained, such as those shown in Figures 3.15 and 3.16 below each AFM image. It can be hypothesized that these rooftop-like lines may have initially formed during epitaxy, following the substrate terraces. Due to the high roughness and inhomogeneity of the Ge surface, the available growth area likely promotes a random nucleation pattern, which results in a wide range of measured d values. Ultimately, the areas exhibiting the highest degree of darkness are postulated to correlate with the presence of TD (yellow arrow).

Finally, when examining large-scale oscillations in the signal (such as profiles and images), which are due to strain-modulated growth, the samples t120 and T175 distinctly exhibit the most pronounced hills. On average, these hills are spaced around 1000 nm. Relating this to the previous analysis, the RAS signals discussed in section 3.1 were unable to differentiate these oscillations from those of the other three samples. This confirms that the surface roughness is not sufficiently degraded to cause deviations in the linear progression of the reflectance signal, as analyzed in Figure 3.4. This may indicate that the larger surface features observed in the t120 and T175 samples could be associated with the regions of higher misorientation (green areas) shown in Figures 3.5 and 3.6. However, the remaining samples do not exhibit similarly large features or display a comparable distribution of misorientation as the rest of the t-batch samples or the T-batch samples. Consequently, the variability in surface morphology and the extensive time required to scan additional areas result in an ambiguous pattern, complicating the ability to draw definitive conclusions. Furthermore, the occurrence of large-scale oscillations appears to correlate with the elevation of RMS roughness, as indicated in Tables III.IV and III.V. This association is likely influenced by the heightened strain concentrations within these hills.

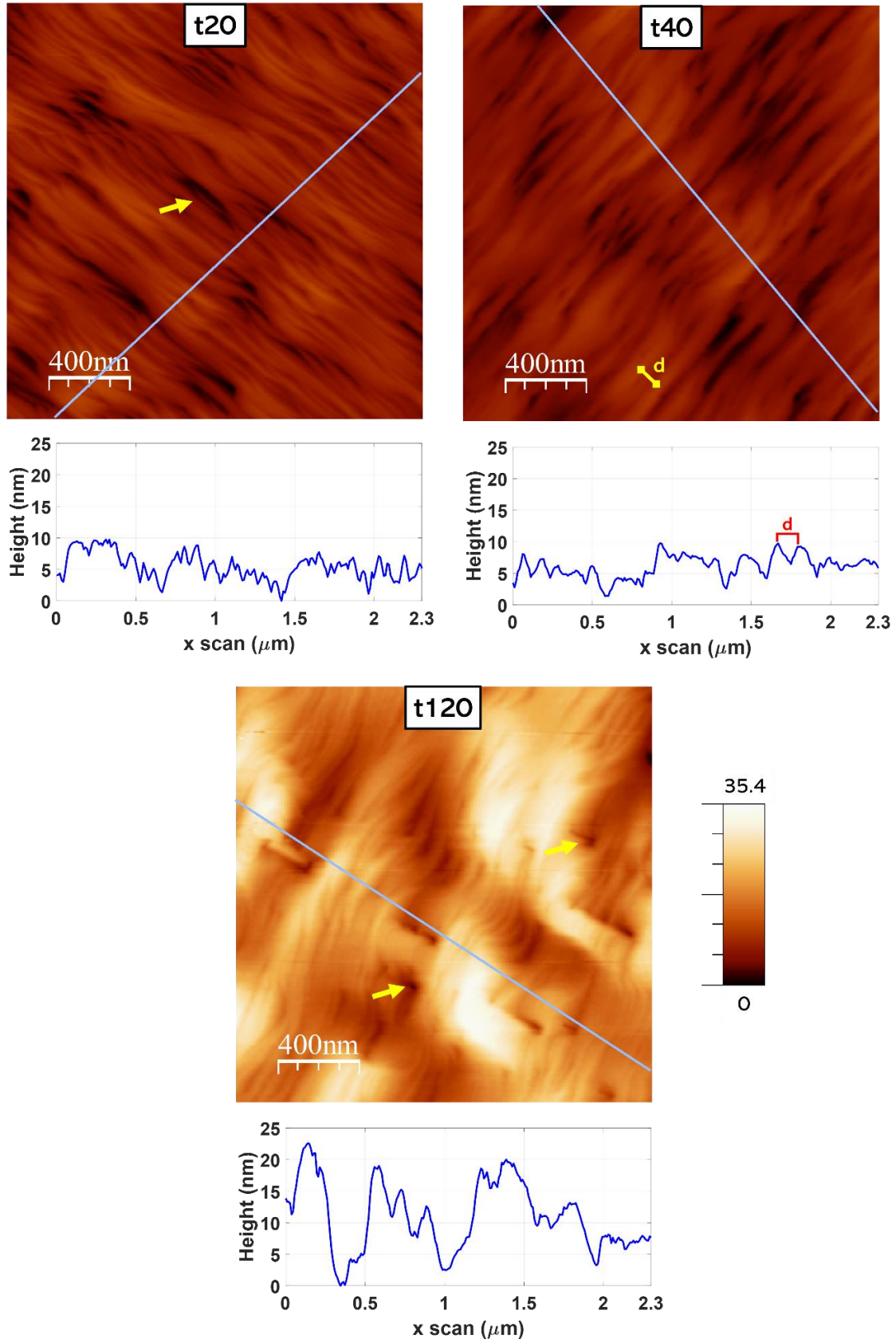


Figure 3.15. AFM images ($2 \times 2 \mu\text{m}^2$) depicting selected t-batch samples. The accompanying profiles represent cross-sectional blue lines marked on the respective AFM images. The parameter d denotes the distance between the peaks of the surface features. Yellow arrows indicate the presence of TD.

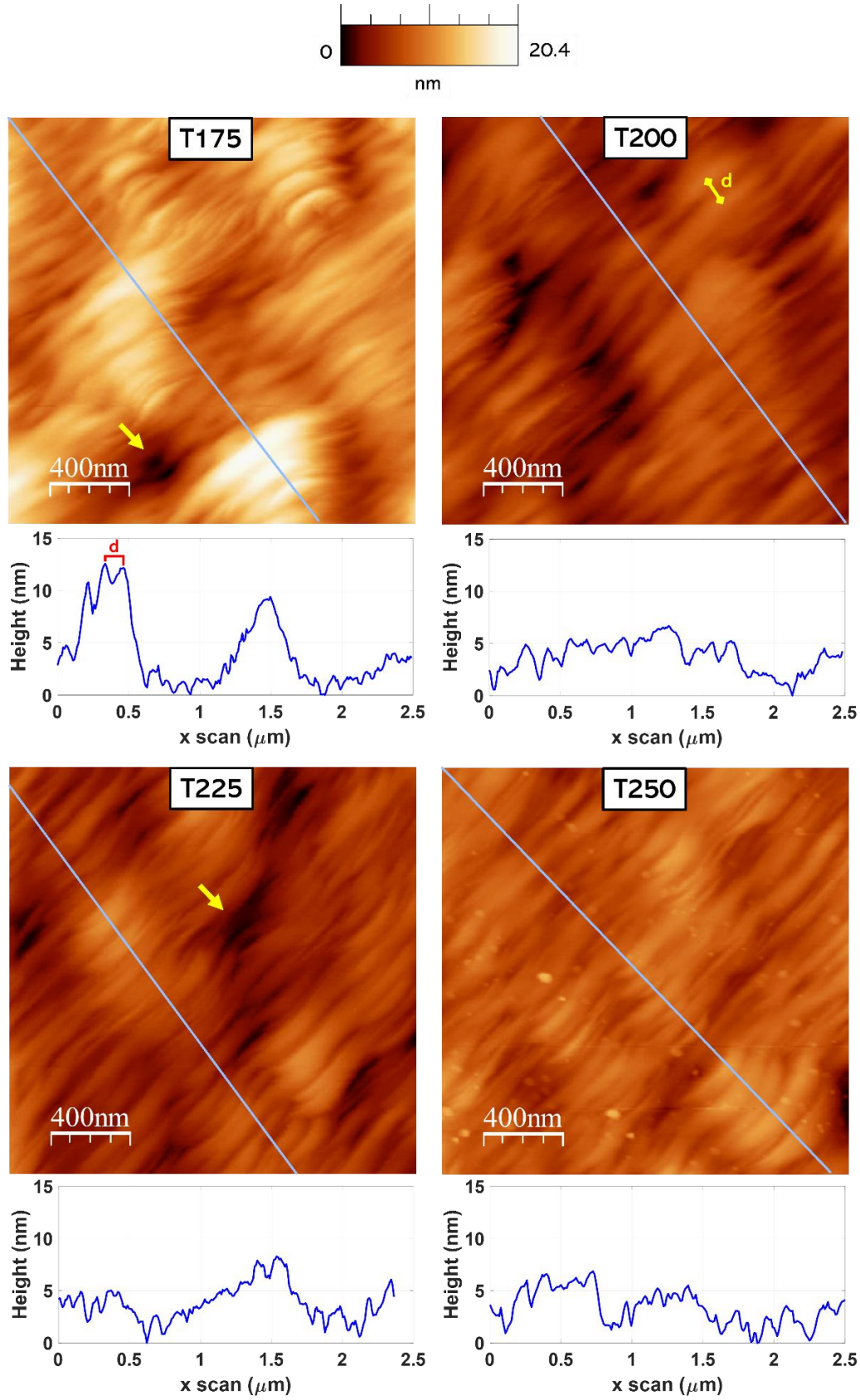


Figure 3.16. AFM images (2x2 μm^2) depicting the T-batch samples. The profiles shown below the images represent cross-sectional blue lines marked on the corresponding AFM images. The parameter d indicates the distance between the peak lines, while yellow arrows indicate TD.

3.5 Discussion and conclusions

This section presents the final conclusions and discussions, aiming to synthesize and integrate the key points discussed in the preceding sections of Chapter 3.

- **In-situ measurements during the MOVPE growth process:** RAS measurements have indicated that the surface morphology and reconstruction of the t-batch and T-batch samples differ from the reference sample (standard Ge substrate), as evidenced by their generally lower signal intensity. However, RAS alone is insufficient to draw definitive conclusions, and additional external characterization techniques have been required to suggest that the RAS signal may reflect suboptimal morphology, at least for epitaxial purposes.

Despite this, some insights can be gleaned from the RAS data. For example, the t-batch samples exhibit sensitivity due to variations in Ge thickness. This, combined with the presence of Si beneath the Ge, can alter the dynamics of the Fabry-Pérot oscillations observed in these measurements. Furthermore, surface and Ge|Si interface roughness, coupled with varying Ge thickness, complicate the assessment of sample quality. The T-batch measurements (constant Ge thickness) corroborate the sensitivity of RAS to Ge thickness, as evidenced by their virtually identical RAS signal.

Comparison to Ge standard substrate measurements is limited, beyond the observations noted, due to the different miscut angles of the Ge standard substrates (6° towards (111)) and the Ge|Si virtual substrates (5° towards (111)). This difference in miscut angles likely affects the RAS signal from surface reconstruction in these two orientations, making comparisons to the reference sample illustrative.

- **Lattice deformation:** EBSD analysis utilizing KAM maps has revealed a significant level of strain in both batches of samples. The misorientation and plastic deformation within these batches are not homogeneously distributed. This observation correlates with the unfavorable TDD and RMS roughness values presented throughout this chapter. The observed inhomogeneity likely arises from lattice relaxation due to uneven stress

distribution and the inherent material anisotropy. The uneven stress distribution likely contributed to the anomalous 50° cross-sectional line-like defect, which was more perceptible in sample t20. However, the insufficient number of surface measurements conducted suggests that this discrepancy may be occasional. Additionally, both t40 and T175 exhibit identical growth processes when the impact of the cleaning methods is disregarded. These samples share the same inhomogeneity in misorientation. This characteristic is consistent with the other samples within the T-batch, indicating that variations in growth temperatures do not appear to significantly influence the quality of the layer.

As shown in the Ge/Ge structure, plastic deformation is lower but still visible using EBSD. Similar to the Ge/Si structures, the misorientation distribution remains heterogeneous. This is evident from the presence of dislocations, which, although reduced, are still observable in ABF-STEM images. These findings suggest that the growth method employed does not yield a surface with high morphological quality, leaving residual stresses in the resulting virtual substrate.

- **Interface analysis:** The TEM images presented in this section indicate a very high linear misfit dislocation density at the Ge|Si interfaces in samples t20 and t140. Specifically, the linear density of misfit dislocations in sample t40 is approximately 11% lower compared to that in sample t120. This slight reduction in dislocation density in t40 could suggest the presence of regions free from defects. Higher magnification of the Ge|Si interface highlights areas where dislocations fully penetrate the layer and reach the surface, thereby confirming the presence of deformation and surface defects. This observation is consistent with the findings depicted in the EBSD and ECCI images.
- **Effect of MOVPE thermal load on Ge surface:** The findings presented in this section indicate that thermal treatment alone contributes to the smoothing of the Ge surface, as evidenced by the RMS roughness values of samples that included a MOVPE growth of Ga(In)As/GaAs layers (later removed), which align with those of samples exposed solely to thermal treatment. At present, only hypotheses can be proposed to elucidate this

phenomenon. One possibility is that annealing in Ge layers deposited on Si substrates can reduce TDD [63], thereby decreasing the number of disruption points on the surface caused by these dislocations. The thermal load involves high temperatures, which might contribute to this effect. However, our Ge layers are only a few nanometers thick, providing insufficient space for TD self-annihilation. Another possibility to consider is that the applied thermal load on the Ge|Si virtual substrates, in combination with elements introduced from the reactor wall, results in a reaction that smoothens the surfaces. This reaction could be due to the interaction of these elements with the Ge atoms, leading to a reorganization that reduces surface roughness. Alternatively, it is possible that the thermal load itself provides sufficient energy to the superficial Ge atoms, enabling them to move more freely and reposition themselves into more stable configurations. This atomic mobility can lead to a smoother surface as the atoms find energetically favorable positions, minimizing surface irregularities. Therefore, the smoothing effect observed may be attributed to the combined influence of thermal activation and chemical interactions during the thermal processing.

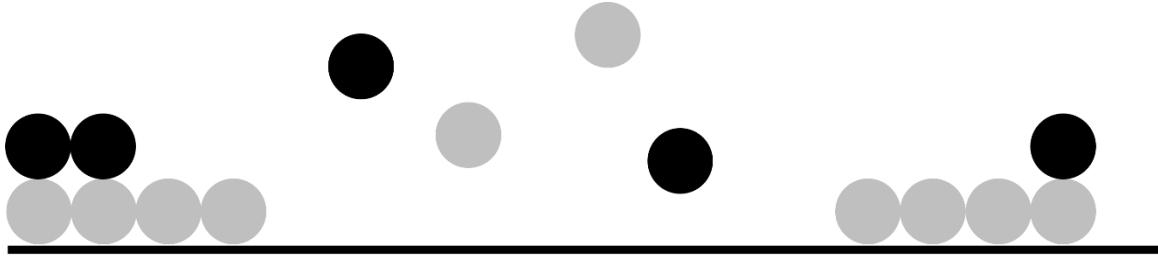
- **Threading dislocations impact on III-V layers:** TEM and ECCI imaging analyses have demonstrated comparable TDD values derived from these two techniques. The TDD values calculated from TEM range from approximately $4 \cdot 10^9$ to $6 \cdot 10^9 \text{ cm}^{-2}$, while ECCI yields values between $3 \cdot 10^9$ and $5 \cdot 10^9 \text{ cm}^{-2}$. However, as detailed in the relevant section, it is important to remember that the TDD values obtained from ECCI may be up to four times higher because the visible spots may represent a lower limit of the TDD.

Referring back to the lifetime calculations presented in section 1.2.3.3, with an average TDD of $5 \cdot 10^9 \text{ cm}^{-2}$ in a typical n+p front junction for GaAs and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ and a doping concentration of 10^{17} cm^{-3} , the resulting τ are observed to be less than tenths of a nanosecond for both GaAs and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$. These values indicate a significant degradation of the carrier lifetime, considering that GaAs and $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ with low TDD typically exhibit lifetimes of a few ns to several tens of ns [154], [155]. Regarding the saturation current density of solar cells made with this material described in Eq. 1.8, it can increase by several orders of magnitude, resulting in a significant reduction in the cell voltage. To mitigate

TDD in active subcells, a dislocation filter layer can be deposited. However, achieving a reasonable TDD ($\sim 10^6 \text{ cm}^{-2}$) requires above 5 μm of dislocation filter layer [74], significantly increasing material costs.

Finally, although the t120 sample appears to exhibit a lower TDD, strain analysis (Section 3.2) and TEM images (Sections 3.3 and 3.4) indicate otherwise. This discrepancy suggests that additional measurements are necessary to improve accuracy and resolve any inconsistencies.

- **Study of Ga(In)As surface morphology:** Based on the d values and by comparing these to the distances corresponding to the step heights of one or two atoms (refer to the values provided in the corresponding text in section 3.4.1), it can be hypothesized that these rooftop-like lines may have initially formed during epitaxy process, following the substrate terraces. Due to the high roughness and inhomogeneity of the Ge surface, the available growth area likely promotes a random nucleation pattern, which results in a wide range of measured d values.



Performance characterization of triple junction solar cells on GON substrates

CHAPTER 4

Thus far, we have focused on studies involving Ge|Si virtual solar cells and standard Ge substrates. In this section, we explore the applicability of GON substrates for GaInP/GaInAs/Ge TJSCs in a work in collaboration with *IMEC* and *UMICORE* (Belgium). The objective of employing these alternative substrates is to enable the reusability of Ge wafers. The preparation and processing of these GON substrates have been detailed in section 1.2.4.3, with further elaboration available in other sources [156]. Briefly, a thin foil—supported by micropillars—from the Ge wafer is prepared for various electronic applications, including solar devices, as discussed in this chapter. For instance, this foil can be used for these applications either before or after detachment from the wafer following semiconductor epitaxial deposition. In our case, we employ detachment after MOVPE growth. Regardless, after detachment, the Ge substrates can be reconditioned and reused for subsequent epitaxial growths. Prior to proceeding further, the results will be presented concisely in accordance with the chapter's structure, followed by a brief section summarizing the conclusions.

For the fabrication of GON wafers by *UMICORE*, *IMEC* (Belgium), a 200-mm 6° offcut towards (111) Ge wafer from was utilized. The wafer was patterned using deep-UV lithography followed by dry etching to create an array of straight columnar pores. Subsequently, the patterned wafer was placed in a load-locked chemical vapor deposition reactor. An annealing process was conducted in a reducing environment at 730 °C and 1 atm H₂, which restructured the wafer surface within a few minutes. This process resulted in the formation of a GON structure with a perfectly coalesced surface.

Before explaining the specific characteristics of the provided samples, it is essential to outline their preparation process. The porosification or creation of micropillars must be designed to withstand delamination, as these micropillars must endure mechanical stresses (such as handling the wafer manually or bearing the weight of the deposited III-V material), high temperatures, and pressure variations. Generally, a higher micropillar density correlates with increased resistance, particularly to mechanical stresses.

The samples were prepared using a specific mask to create the patterns (details of which are not disclosed due to intellectual property concerns). The nomenclature for these samples follows the convention described in [156], where each sample is assigned a name that includes an 'F' followed by a number. This naming scheme references a baseline sample where a detachment force (F) is defined as the unit (1). For example, samples named F200 can withstand a detachment force 200 times greater than that of the baseline F1 sample. In simpler terms, a higher number indicates a denser array of micropillars, thereby providing greater resistance to stress.

The samples provided were designated as F200, F1500, and F5000. The Ge foil in all examined samples is 7 μm thick, comprising a 6 μm boron-doped Ge epitaxial layer with a boron

concentration of $6 \cdot 10^{17} \text{ cm}^{-3}$, grown on a Ga-doped GON substrate with a gallium concentration of $5 \cdot 10^{17} \text{ cm}^{-3}$. Initially, a 200 mm diameter wafer was downsized using a laser to dimensions of $7 \text{ cm} \times 7 \text{ cm}$ to fit within the epitaxial reactor.

These substrates were used to grow TJSC structures. No preliminary cleaning step was performed on the samples. The device structure includes a GaInP nucleation layer, followed by a GaInAs overbuffer layer, serving as a template for the growth of GaInAs and GaInP subcells, which are interconnected by tunnel junctions. This structure is based on a design similar to that described in [83]. The GaInAs middle cell is optically thick, whereas the GaInP top cell is thinned to achieve a current-matched configuration suitable for the AM0 solar spectrum. The overall thickness of the III-V semiconductor structure is approximately $5.5 \text{ }\mu\text{m}$. For the epitaxial growth process, the precursor gases used for group-V elements are AsH_3 and phosphine PH_3 . For group-III elements, the precursors include TMGa, TMAI and TMIIn. The doping of the layers is carried out using DETe and DTBSi for n-type materials, and DMZn and CBr_4 for p-type materials. Photovoltaic devices with an active area of 0.1 cm^2 were produced utilizing conventional photolithography methods and electroplating of gold. Isolation of the devices was accomplished through wet etching to form mesa trenches. These solar cells were fabricated without the application of ARC.

4.1 In-situ measurements during epitaxial deposition

Firstly, the nucleation of GaInP on the GON substrates was assessed by comparing the RAS signatures obtained. Figure 4.1 illustrates the RAS signatures observed during the nucleation of GaInP on both types of substrates. Based on the RAS data analysis, it is evident that the signatures exhibit a high degree of similarity and demonstrate a high-quality nucleation.

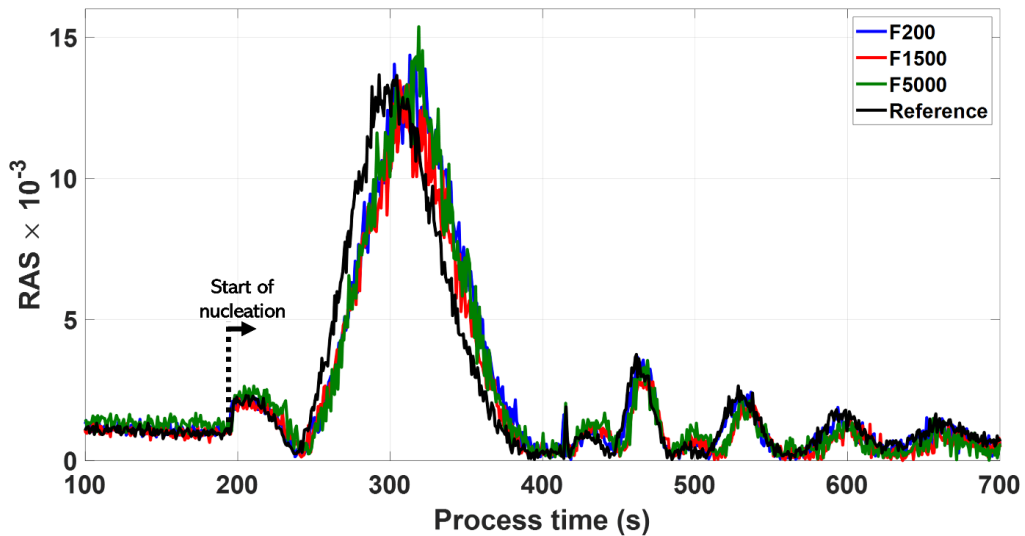


Figure 4.1. RAS signatures measured at 2.1 eV in transient mode during the nucleation of the GaInP layer on the Ge surface, comparing a standard Ge (reference) substrate with GON-treated samples.

4.2 Electrical characterization

The EQE of the completed TJSC devices was evaluated without the use of an ARC. The results of these measurements are illustrated in Figure 4.2. The EQE of the GaInP top cell demonstrates a consistent response across all samples, remaining within the bounds of measurement uncertainty. In contrast, the EQE of the GaInAs middle cell exhibits variations in the interference fringes, attributable to minor differences in layer thicknesses. A notable deviation is observed in the F200 sample (blue), which displays a reduced average EQE. For the Ge bottom cell in the GON samples, the EQE in the long wavelength region is lower compared to the baseline, corresponding to a thinner Ge layer (7 μm in the GON samples versus 170 μm in the reference samples on standard Ge substrates).

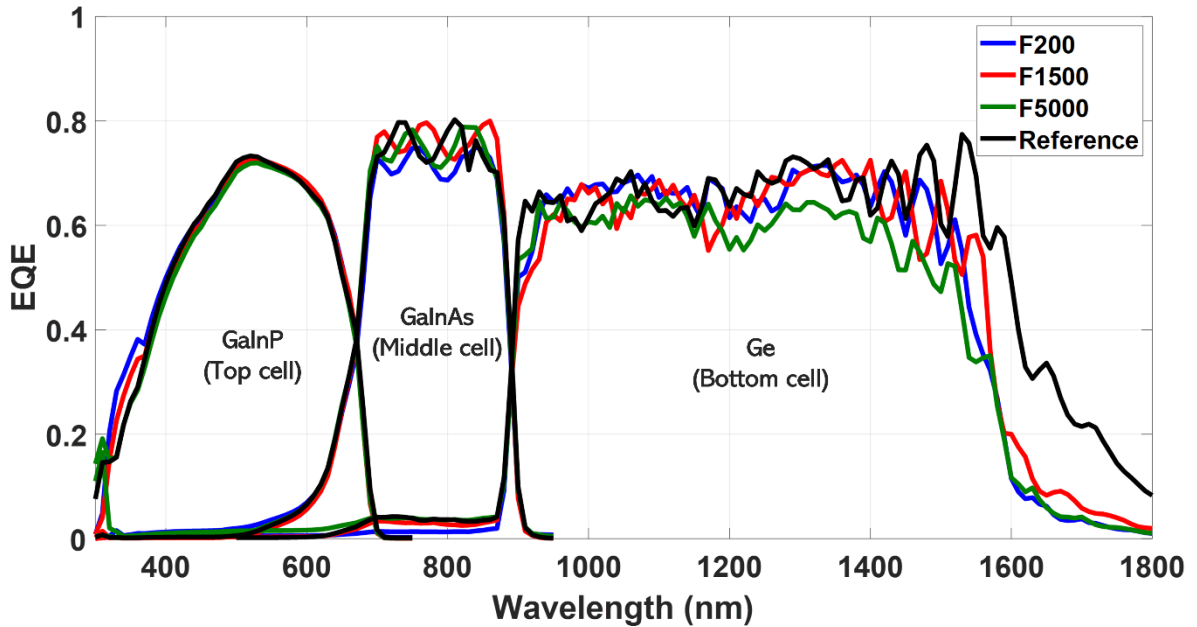


Figure 4.2. EQE of TJSCs grown on standard Ge substrates and GON samples.

The J–V characteristics of the TJSC solar cells were systematically evaluated across multiple devices, as depicted in Figure 4.3. The observed $\sim 10\%$ variation in the J_{sc} in the illuminated J–V curves are primarily attributed to differing shadowing factors among the devices. Comparative analysis of J_{sc} between reference and GON samples reveals similar values. The V_{oc} for the TJSC grown on GON shows a marginally lower value by approximately 30 mV. The F200 sample exhibits a notably reduced V_{oc} (approximately 0.3 V) in comparison to both the reference sample and the other GON samples (F1500 and F5000). Detailed explanations for these observations will be presented in the concluding section.

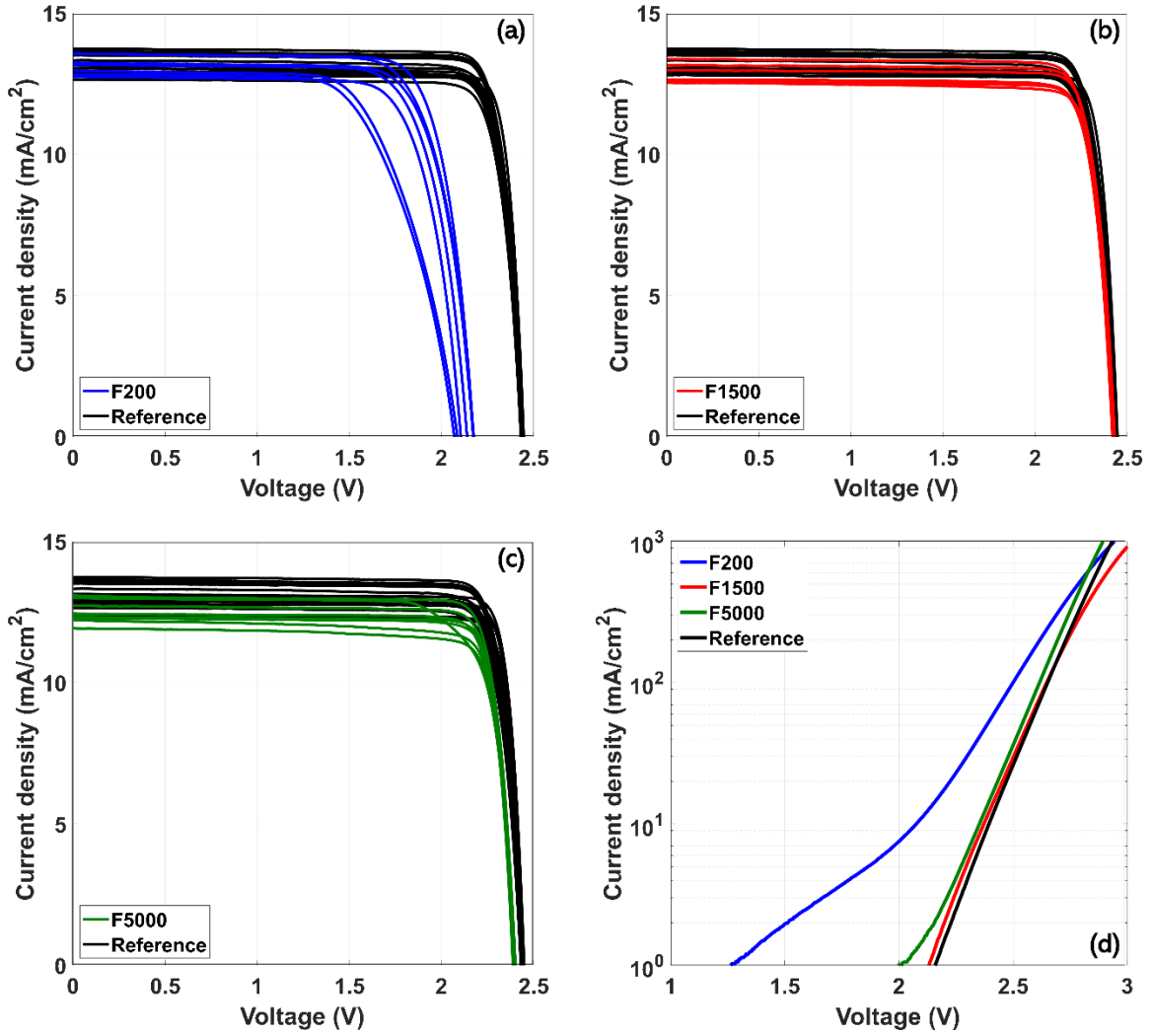


Figure 4.3. Light and dark J-V characteristics for each GON sample compared to the reference sample (standard Ge substrate). (a) Comparison between F200 and the reference sample, (b) F1500 and the reference sample, (c) F5000 and the reference sample, and (d) dark I-V curves of all samples for direct comparison.

4.3 Solar device detachment

As outlined in the introductory section of this chapter, the primary objective of this novel substrate design is centered around its reusability, primarily facilitated by the potential detachment of the Ge foil. Initially, the approach involved manually transferring the stack onto Kapton tape. A test structure comprising a 7- μm Ge foil (F1500) with an MOVPE-grown III-V stack was transferred onto freestanding Kapton tape (see Figure 4.4(a)). While the entire foil area was successfully detached, the tape's limited radius of curvature caused perpendicular cracking relative to the detachment direction. To mitigate this issue, a different method was attempted with another processed piece from the F1500 samples. In this case, the Kapton tape was affixed to a glass slide to prevent curvature-induced cracking during peeling.

However, this adjustment inadvertently reduced the peeling pressure at the crack front, resulting in incomplete detachment of the foil (see Figure 4.4(b)).

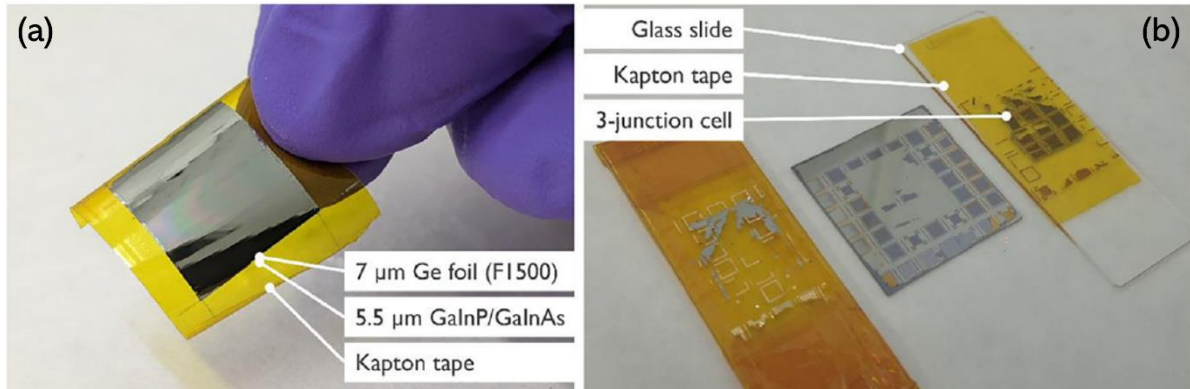


Figure 4.4. (a) Transfer of III-V/Ge stack of the sample F1500 onto freestanding Kapton tape using manual methods. (b) Solar cells transferred in two stages onto Kapton tape affixed to a glass slide. The glass slide mitigated bending and cracking of the layers but resulted in reduced peeling pressure at the crack front, thus preventing complete detachment in the initial attempt.

4.4 Discussion and conclusions

The present section will sum up and analyze the findings and discussions elaborate upon in the prior chapters.

- **In-situ measurements:** The striking similarity in the RAS signal depicted in Figure 4.1 suggests that there are negligible distinctions in surface reconstruction during the nucleation phase between the conventional Ge substrates (reference) and the GON-treated samples. This observation may imply that the surface characteristics of these novel samples closely resemble those of the standard Ge wafers.
- **Electrical characterization:** In terms of electrical characteristics, the consistent GaInP signal observed in Figure 4.2 underscores the exceptional quality of the Ge surfaces used in the TJSC, evident from its close resemblance to the reference signal. The marginal decrease in GaInAs EQE observed in F200 (blue) is likely attributed to inadvertent aging of the GON surface during sample preparation. This aging could have introduced macroscopic defects during MOVPE deposition, potentially causing partial shunting of the solar cell devices. Furthermore, the different EQE response of the Ge bottom cell at longer wavelengths suggests that photon reflection at the Ge/air interface behind the GON samples may mitigate this reduction by offering a secondary opportunity for light

absorption. Nevertheless, the observed response across all scenarios exceeds the requirements for a Ge bottom cell in TJSCs intended for space applications.

In reference to Figure 4.3, the observed 30 mV reduction in V_{oc} is more favorable than anticipated, especially considering the 7- μm thick Ge bottom cell in these configurations. This thinner Ge layer is prone to increased back surface recombination due to its larger surface area-to-volume ratio in the micropillar regions, contrasting with standard Ge substrates that typically feature a 170- μm thick bottom cell. The approximately 0.3 V decrease in V_{oc} for the F200 sample can be attributed to the previously discussed issue of Ge surface aging. This degradation of the Ge surface introduces additional recombination pathways in the solar cells, as evidenced by the different ideality factor observed in the dark J–V curves. Mitigating this effect requires strategies to maintain surface integrity, thereby optimizing cell performance. Moreover, enhancing the V_{oc} of the Ge subcell in GON samples could be achieved through effective back surface passivation post-detachment from the parent substrate.

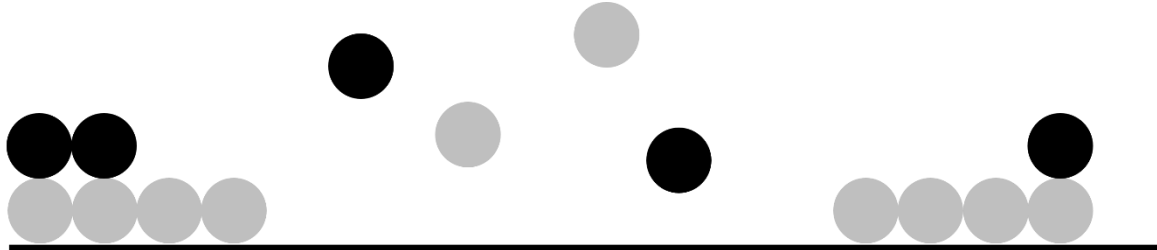
In conclusion, the production of TJSC on GON substrates yields performance outcomes nearly indistinguishable from those achieved on conventional Ge substrates. This underscores the capability of these thin Ge epitaxial layers on GON substrates to serve as viable alternatives to thick Ge wafers for both bottom cell applications and as seeding material for the fabrication of III–V multijunction solar cells.

- **Solar device detachment:** The observed partial detachment during the second transfer (Figure 4.4(b)), resulting in device damage, highlights a critical challenge that needs addressing for successful reusability. However, the initial successful detachment in the first attempt (Figure 4.4(a)) demonstrates potential for reusability applications once this issue is effectively resolved. Further optimization of the transfer process, potentially including refinement of micropillar fabrication techniques, is necessary to mitigate detachment-related damage and enhance the overall reliability of the method for future applications.

As concluding remark, the first attempts at growing full TJSC on the GON substrates are encouraging, with a cell performance very close to the baseline on standard Ge. Further steps would include the optimization of the GON template to enable an efficient detachability and compatibility with the MOVPE process, while maintaining a high robustness for processing of the solar cell devices.

Block II

Study of diffusion in Ge



Solid state diffusion in Ge

CHAPTER 5

A thorough awareness of dopant diffusion mechanisms is fundamental for understanding how junction regions within solar cells (the emitter and base) are formed. Therefore, comprehending dopant diffusion processes is necessary for optimizing the design and fabrication of solar cells. Hence, in this section, we explore one of the most common donor dopants in Ge through MOVPE processes, beginning with an introduction to its diffusion mechanisms.

5.1 Introduction

The diffusion coefficient, or sometimes diffusivity, is the factor of proportionality linking the flow density of diffusing atoms with the concentration gradient. This relationship is typically given by the Arrhenius equation:

$$D = D_0 e^{\frac{E_a}{k_B T}} \quad (\text{Eq. 5.1})$$

The pre-exponential factor D_0 can be interpreted as a jump frequency factor. There are various diffusion mechanisms [157] contingent upon whether the diffusing atom occupies a lattice position (substitutional) or an interstitial site. By exchange with a direct neighbor, a substitutional atom can migrate, whereas an interstitial atom can jump from an interstitial site to a nearest neighbor site. In addition to these, the vacancy mechanism, widely acknowledged as the dominant diffusion process in Ge [158], involves a diffusing atom jumping to a neighboring vacancy lattice site. The energetic intricacies of this migration process entail the H_m , influenced by factors such as electrostatic forces and the Fermi level in the bulk. Prior to any migration, punctual defects, including vacancies, must be generated, each possessing an associated H_F . Thus, the activation energy can be expressed as $E_a = H_m + H_F$. Figure 5.1 illustrates the energy jump for the diffusing atom to change position in the lattice when H_m is surpassed.

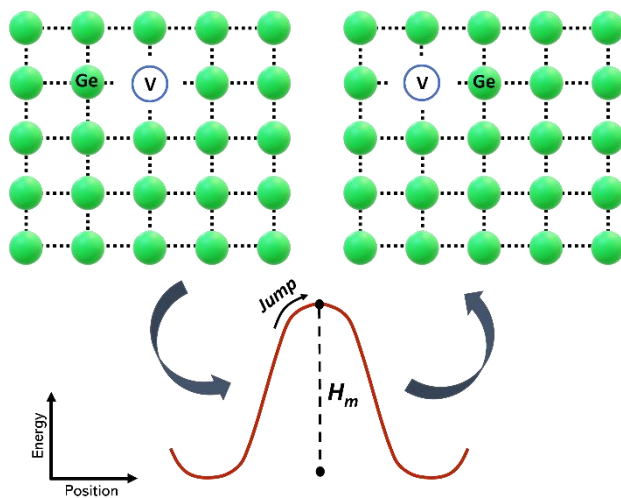


Figure 5.1. Vacancy mechanism for self-diffusion. The labeled Ge atom migrates by jumping to the vacancy to its right once the value of H_m is exceeded. The green spheres represent Ge atoms and the blue circles represent vacancies.

The diffusion coefficient is typically a sum of contributions from interstitial and vacancy mechanisms, as expressed in Eq. 5.2:

$$D_{Ge} = D_0^I e^{\frac{E_a^I}{k_B T}} + D_0^V e^{\frac{E_a^V}{k_B T}} \quad (Eq. 5.2)$$

In the case of Ge, self-diffusion predominantly adheres to the monovacancy mechanism [159]. Accordingly, the interstitial term in Eq. 5.2 becomes negligible, allowing the diffusion coefficient or diffusivity to be expressed as a product of the diffusion coefficient D_V and C_V^{eq} :

$$D_{Ge} \cong D_0^V e^{\frac{E_a^V}{k_B T}} = f_V D_V C_V^{eq}(T) \quad (Eq. 5.3)$$

In Eq. 5.3, f_V is equal to $1/2$ for the monovacancy mechanism in the diamond Ge lattice. Yet, the monovacancy in Ge may exhibit different charge states. If the vacancy can exist neutrally (0), as a singly positive (donor, -), or singly negative (acceptor, +) entity, the overall equilibrium concentration of vacancies is influenced by the Fermi level in the material [157]. This introduces a dependency on the doping density, making the self-diffusion coefficient not only a function of temperature but also reliant on the Fermi level for highly doped, extrinsic material. When considering different charge states of the vacancy, Eq. 5.3 becomes [159]:

$$D_{Ge} = D_{Ge}^0 + \sum_{m=1} D_{Ge}^{m-} \left(\frac{n}{n_i}\right)^m + \sum_{s=1} D_{Ge}^{s+} \left(\frac{n_i}{n}\right)^s \quad (Eq. 5.4)$$

Eq. 5.4 incorporates multiple positive and negative charge states, reflecting the interaction of charge carriers. Nevertheless, the experimental self-diffusion coefficient findings can be explained when taking into account only the neutral and negative charge states of the vacancy [160]. In practical terms, this implies:

$$D_{Ge} = D_{Ge}^0 + \sum_{m=1} D_{Ge}^{m-} \left(\frac{n}{n_i}\right)^m \quad (Eq. 5.5)$$

The following sections will discuss this equation more extensively, revealing its implications on different diffusion mechanisms that depend on the doping characteristics of the material.

5.1.1. Modeling of the diffusion phenomenon

Simulations aid in comprehending the process of diffusion by reproducing the motion of atoms within the bulk semiconductor. Particularly, utilizing Eq. 5.5 can lead to unknown combinations of charge states that may not be readily apparent. Before delving into the numerical methods employed, a clear explanation of the PDE governing diffusion is necessary. The equation is defined as follows:

$$\frac{\partial U(x, t)}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial U(x, t)}{\partial x} \right) \quad (\text{Eq. 5.6})$$

For the case under study, two aspects need consideration. First, Eq. 5.5 was originally formulated for self-diffusion but, as explained in following chapters, dopants are bound to the V_{Ge} that play a pivotal role in the diffusion throughout the semiconductor [161]. Second, the diffusion coefficient is concentration-dependent, namely, $D = D(U)$, owing to the strong correlation between n in Eq. 5.5 and the doping level. Thus, D cannot be extracted from the spatial derivative as a constant, making the equation non-linear. The difficulty lies in the imprecise knowledge of the concentration distribution. The application of the chain rule is necessary to facilitate the computation of Eq. 5.6. For brevity, the variable dependencies of U are omitted:

$$\frac{\partial U(x, t)}{\partial t} = \frac{\partial D(U)}{\partial x} \frac{\partial U}{\partial x} + D(U) \frac{\partial^2 U}{\partial x^2} = \frac{\partial D(U)}{\partial x} \frac{\partial U}{\partial U} \frac{\partial U}{\partial x} + D(U) \frac{\partial^2 U}{\partial x^2} \quad (\text{Eq. 5.7})$$

Simplifying

$$\frac{\partial U}{\partial t} = \frac{\partial D(U)}{\partial U} \left(\frac{\partial U}{\partial x} \right)^2 + D(U) \frac{\partial^2 U}{\partial x^2} \quad (\text{Eq. 5.8})$$

$D(U)$ is known but the quadratic spatial derivative hinders an analytical solution to this expression. Then, resorting to numerical methods becomes a necessity for advancing the understanding of the diffusion process. The numerical methods utilized for these simulations are described in Appendix A. Furthermore, a comparative analysis of the numerical methods employed to ensure reliable results is presented therein. Interested readers are encouraged to refer to Appendix A for further details.

5.1.1.1 Identification of profiles for different concentration-dependent diffusion coefficient

As elucidated earlier, the diffusion coefficient D is intricately linked to the electron density within the Ge bulk (Eq. 5.5). Therefore, the experimental profile of D exhibits variability dependent on the profile of dopants. Consequently, it proves highly advantageous to visualize the potential profiles, not of Ge or V_{Ge} alone, but rather those of the donor dopants which, as previously mentioned, traverse the lattice in conjunction with V_{Ge} . The chosen spectrum of charge states of V_{Ge} spans from 0 to 3-, guided by literature insights suggesting the absence of charge states beyond 3- in absolute value for this specific category of dopants [162]. These values of charge state entail representing diffusivity in various forms, including constant (0), linearly dependent (1-), quadratic (2-), and cubic (3-), thereby encompassing a range of

mathematical expressions to characterize the diffusional behavior under different conditions. It is important to know that the diffusivity utilized in Eq. 5.5 exclusively retains the dependence on the associated charge state for generality. For example, in the case of a charge state of 2-, both the constant term and the linear term are null. In Figure 5.2, the distinctive shapes of the donor profiles obtained assuming these possible cases of diffusivity are presented, offering a perception of the spatial distribution of dopants within the Ge lattice. This figure will serve simply as a visual reference for the ensuing chapters, particularly when experimental profiles are presented. It will be useful in correlating and contextualizing the experimental data, allowing for an understanding of the results as they are analyzed and discussed in the subsequent sections. The distinctive feature discernible from this graph, crucial for identifying potential experimental profiles, lies in the different shapes observed as the concentration begins to decline. Specifically, a higher charge state in absolute value corresponds to a more abrupt drop-off in concentration at some depth, as indicated in the figure.

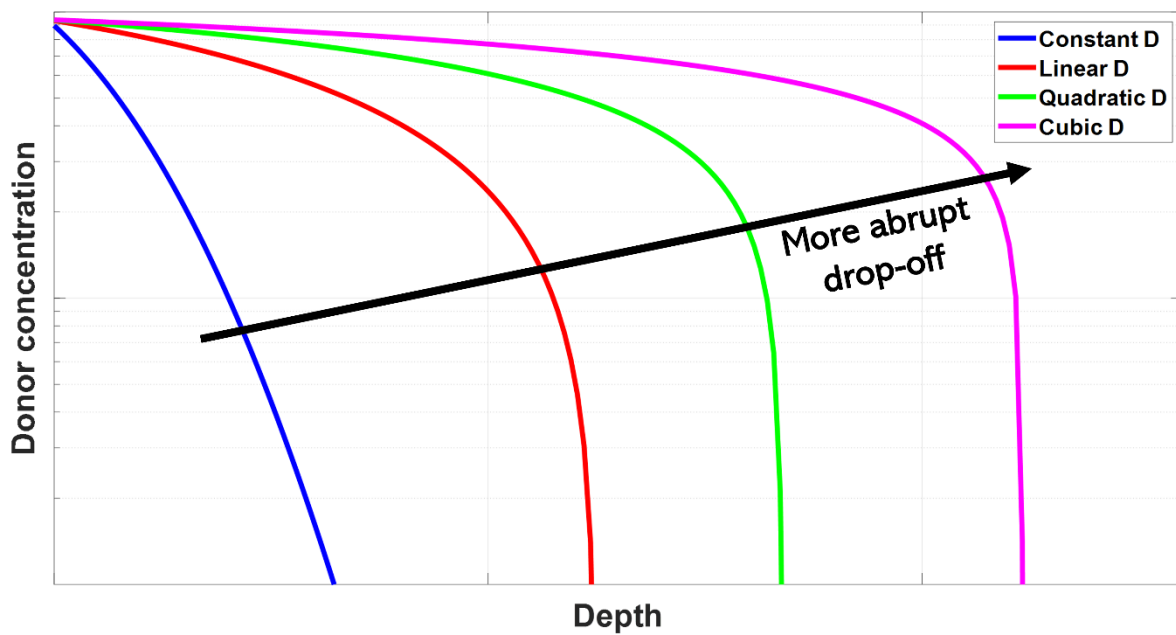


Figure 5.2. Graphical representation of simulations featuring different concentration dependencies. Profiles of donor concentrations depicted by colored lines representing different diffusion scenarios: constant diffusivity (blue), linear concentration-dependent diffusivity (red), quadratic concentration dependence (green), and cubic concentration dependence (magenta). The arrow direction indicates the trend of a more abrupt drop-off in profile.

5.2 Diffusion of group III and V atoms in Ge

5.2.1 Group III in Ge

The different behavior of group III elements (Al, Ga, and In) as solutes in Ge stems from their distinguished ability to form robust covalent bonds with the lattice atoms. Unlike elements from other groups, except for group V, group III elements tend to exist in the substitutional form within the Ge lattice. However, the diffusion of group III atoms in Ge occurs in conjunction with a vacancy [163]. As discussed in the preceding chapter, V_{Ge} typically exhibit a neutral or negative charge state. Likewise, this charge state aligns with that of a group III acceptor in Ge. Consequently, the electrostatic forces between group III atoms and vacancies become repulsive, hampering their binding and subsequent diffusion [164]. Hence, the diffusivity of group-III elements in Ge is relatively small compared to group-V elements.

An alternative interpretation of this phenomenon can be gleaned from Eq. 5.5. With an increase in p-type doping, there is a concurrent decrease in electron concentration. Thus, the right term in this equation diminishes to the extent that only the concentration-independent term remains valid. Certainly, it is important to note that the value of this term will differ compared to the case of purely intrinsic germanium, as it is influenced by the interaction between the dopant and V_{Ge} . As previously shown in Figure 5.2 for constant D , it leads the shape of the doping profile to follow $erfc$ function (blue solid line). To provide a sense of the order of magnitudes involved, Table V.I presents the values for the most typical Group III atoms.

Element	D_0 (10^3 cm ² /s)	E_a (eV)
Al	1 ± 0.5	3.45 ± 0.04
Ga	1.5	3.5 ± 0.3
In	$5.123^{+5.142}_{-2.566}$	3.51 ± 0.06

Table V.I. Pre-exponential factor and activation energy values of the group III elements in Ge. The documented values for Al, Ga, and In can be found in [165] for aluminum, [166] for gallium, and [167] for indium.

5.2.2 Group V in Ge

Research investigations, both experimental and theoretical, into donor diffusion mechanisms have elucidated that n-type dopants (P, As and Sb) exhibit faster diffusion in Ge through a vacancy-mediated mechanism compared to self-diffusion [168], [169], as Eq. 5.5 indicates with the increase of the electron concentration. This accelerated diffusion of donor atoms

poses a challenge in the context of forming ultra-shallow donor profiles in n⁺p junctions. The significance of ultra-shallow junctions stems from the growing interest in scaling down electronics, where a thin n⁺ region offers increased electron quantities without compromising the recombination characteristics in the lower-doped p-type region. However, achieving high donor doping does not necessarily translate to a completely active dopant profile [170]. Hence, it becomes appropriate to devise effective strategies that mitigate the diffusion of n-type dopants, enhance their electrical activation levels [171], and impede the formation of dopant defect clusters [172]. In PV devices, understanding donor diffusion is intimately linked to the adjustment of emitter/base thickness, as it directly influences the performance of solar devices. For instance, in GaInP/GaAs/Ge TJSCs, it is reported that a thinner emitter leads to higher V_{oc} outcomes [173]. In addition to thickness control, understanding the diffusion behavior of donors is crucial, as their concentration significantly influences the properties of minority carriers [174]. This knowledge is essential because donors and Ge (as well as acceptors) can form alloys near the interface [175], potentially leading to undesirable and uncontrollable regions. These regions may exhibit changes in doping polarization, resulting in parasitic junctions or different phases with unfavorable characteristics for solar devices.

To comprehend and effectively control dopant diffusion and dopant-defect interactions within Ge, it is essential to revisit the characteristics of intrinsic defects. This includes an exploration of their potential charge states, formation and migration enthalpies, as well as their interactions with dopant atoms, as detailed in Section 5.1. Notably, both experimental and theoretical findings underscore the prevalence of vacancies in Ge. The interplay of intrinsic defects, particularly those substitutionally dissolved with foreign atoms, significantly influences the diffusion of dopants. Direct dopant exchange with neighboring host atoms proves to be energetically prohibitive and, thus, lacks relevance in the context of dopant diffusion in Ge. With a focus on V_{Ge} participating in dopant-defect interactions, the ensuing reactions offer a general depiction of dopant diffusion mechanisms in semiconductor materials:



The AV pair, comprising a substitutional donor (A_s) atom and a neighboring vacancy (V_{Ge}), participates actively in the mechanisms underlying dopant diffusion in Ge. Reaction I (R.I) denotes the vacancy-mediated pathways for dopant diffusion, wherein each defect involved can exist in different charge states. The charges of these defects are not denoted by superscripts for clarity. Reaction I defines the effective diffusion of the dopant A_s facilitated by the formation of a mobile dopant-defect pair. In instances where the availability of AV limits

the generation of A_s , the resultant dopant diffusion is termed foreign-atom controlled [176]. Conversely, the native defect-controlled mode ensues when the elimination of V_{Ge} constrains the formation of A_s , impeding its subsequent diffusion. The diffusion behavior of group III and V elements in Ge aligns with the characteristics of foreign atom controlled diffusion.

Within the V-mediated diffusion mechanism, the donor atom must associate with the vacancy. A single exchange in position between V and the donor atom does not lead to net diffusion. In the diamond crystal structure of Ge lattice, the V must approach the donor atom from a different direction and then engage in a position exchange, a phenomenon known as the ring mechanism of diffusion [177]. This process allows the donor atom to advance by one lattice site, and through iterative occurrences, donor atoms can effectively diffuse (refer to Figure 5.3 for a schematic of the ring mechanism of diffusion). A prerequisite for such diffusion mechanisms is the strong binding of the donor atom with the vacancy; otherwise, as V moves away, the donor atom will dissociate. In such cases, the donor atom becomes effectively immobilized, necessitating interaction with another vacancy for further migration.

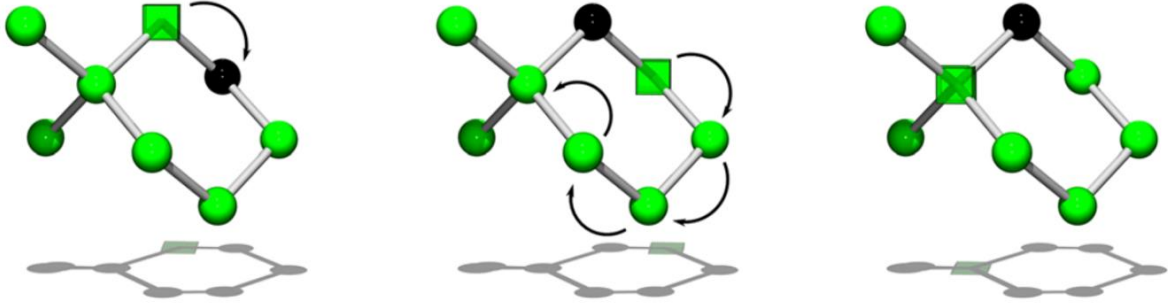


Figure 5.3. Schematic depiction of the ring mechanism of diffusion in the Ge lattice. The diagram features a black sphere representing a single donor, a green square representing V_{Ge} and green spheres portraying the Ge atoms. This representation was sourced from [164].

The determination of activation energy for the diffusion process outlined is computed through the following expression [168]:

$$E_a = H_V^f + \Delta E_{AV}^f + H_{AV}^m \quad (\text{Eq. 5.9})$$

The formation enthalpy is subject to various factors, including the Fermi energy or the total energy of the cell containing the vacancy in a charge embedded in the Ge host lattice [178].

To sum up, the diffusion mechanism of n-type dopants A (P, As, Sb) in Ge is precisely described by the vacancy mechanism, encompassing specific defects and associated charge states:



In this reaction (R.II), r represents the positive charge state of the substitutional donor, while m is the charge state of the V_{Ge} , typically negative under n-type conditions [160], [164]. The diffusion of donor atoms A occurs through the mobility of AV pairs, and upon their dissociation, it results in the generation of substitutional dopants A_s and V . The manifestation of the charge state of the AV pair is evident in the dependence of diffusion on doping, as expressed in Eq. 5.5.

The challenge at hand revolves around the varying values of the charge state associated with V_{Ge} . The predominant charge state is commonly accepted as -2 [162], [164], resulting in a diffusivity with a quadratic concentration dependence. However, less frequent studies have presented different charge states. For instance, in reference [179], an additional level is proposed, linked to the third acceptor level of the free vacancy, specifically the V^{2-}/V^{3-} transition, in addition to the second acceptor level of the free vacancy (V^-/V^{2-} transition). This combination of quadratic and cubic dependencies in the diffusivity yielded satisfactory fittings for phosphorus profiles. Conversely, reference [180] indicates that their arsenic profiles exhibit proper adjustment with a linearly concentration-dependent diffusion constant. Despite these varied perspectives, it is evident that the independent term can be reasonably considered negligible [181]. Table V.II enumerates all the mentioned diffusivities for comprehensive reference. For convenience, the table exclusively presents values for arsenic, focusing on the case studied experimentally in this Thesis. Additional values for other group V elements can be referenced in the provided citations within the paragraph. The experiments cited herein were carried out under various experimental conditions, such as ion implantation or MOVPE. Consequently, these diverse conditions may have led to different diffusion mechanisms due to changes in the thermodynamics of the system under study.

	Linear	Quadratic	Cubic	
m	1-	2-	2-	3-
D_0^m (cm²/s)	$6.2 \cdot 10^{-3}$	32^{+21}_{-13}	6.82	1017
E_a (eV)	1.9	2.71 ± 0.06	2.583	3.217

Table V.II. Pre-exponential factor and activation energy values pertaining to As diffusion in Ge. The corresponding values are referenced as follows: linear concentration-dependent diffusivity in [180], quadratic dependence in [182] and cubic dependence in [162]. The symbol m signifies the charge state of the vacancies.

A quick comparison of Table V.I and Table V.II shows faster diffusion for group V in contrast to group III in Ge. This distinction becomes particularly pronounced when looking at the activation energies, where the numerical impact is substantially greater due to its location

within the exponential term. As will be shown in next sections, this difference in diffusion between group-III and group-V in Ge will have an important effect on the carrier profiles obtained.

5.3 Ge solid-phase cross-diffusion into III-V epilayers

In any epitaxial process, the interplay of various conditions, such as thermal load and atom deposition, creates a dynamic environment where participating atoms can migrate within the same materials or across adjacent layers. When depositing III-V materials onto Ge, the diffusion phenomenon extends beyond the III-V layers into the Ge wafer, involving not only the elements from the III-V layers but also Ge atoms from the substrate diffusing into the upper and in-process layers through the III-V/Ge interface [183] (refer to the representation in Figure 5.4). So, this cross-diffusion process is therefore sensitive to the morphology of the substrate surface [184].

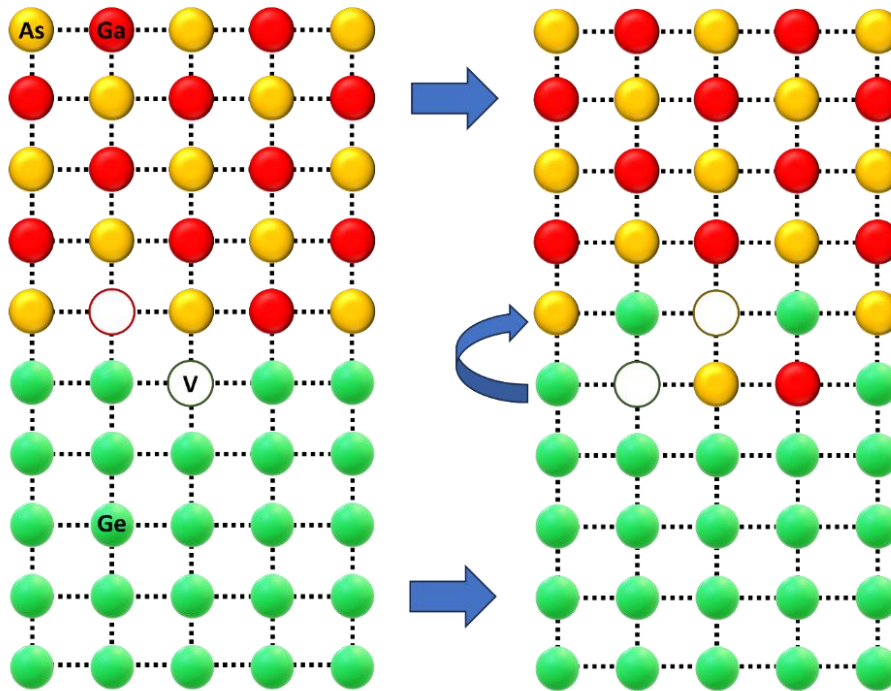


Figure 5.4. Schematic representation of the cross-diffusion mechanism. Ge atoms are represented by green spheres, Ga atoms by red spheres, As atoms by yellow spheres, and vacancies in each layer by white circles. The left image depicts the initial state of the two adjacent layers, while the right image illustrates how atoms diffuse into their corresponding adjacent layers. The choice of GaAs is purely illustrative, as this mechanism can occur for other layers as well.

Ge, when present in GaInP materials, exhibits amphoteric behavior [185], functioning as both a donor and an acceptor within the same material. In GaAs materials, Ge functions mainly as an n-type dopant, while still exhibiting its amphoteric behavior. Regardless of Ge's role, cross-diffusion poses challenges, leading to uncontrolled diffusion into active layers. This cross-

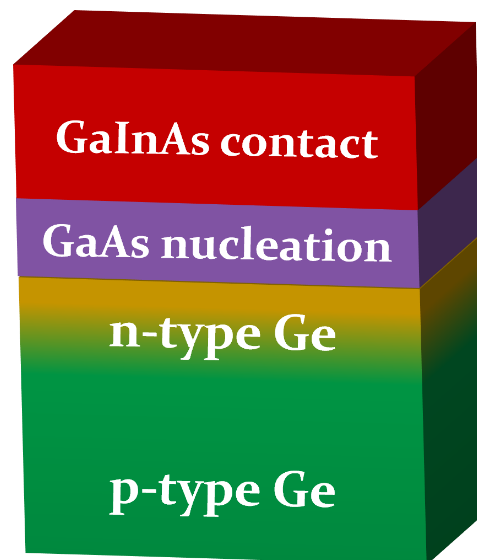
diffusion effect through the interface can result in the formation of uncontrolled pn junctions, adversely affecting the performance of electronic devices [186]. To mitigate this, the deposition of low-temperature GaAs control layers serves as an effective diffusion barrier for Ge [89]. Alternatively, the deposition of a prelayer of As or Ga [89], [187] helps suppress Ge cross-diffusion. Additionally, in any epitaxial process, multiple parameters, including temperature and the V/III ratio during deposition, can be adjusted to influence diffusion dynamics [188].

This elucidation of various diffusion mechanisms in Ge contributes to a comprehensive understanding of potential diffusion dynamics, encompassing discussions on intrinsic point defects, extrinsic diffusion with group III and V dopants, and motivations outlined in the introduction of Section 5.2.2, highlighting the desired applications. The control of Ge/GaAs cross-diffusion is also emphasized, providing insights into the intricate interplay of factors in epitaxial processes.

5.4 Study of the As diffusion in Ge

Before delving into the chapter, it is important to note that it is divided into two parts: the first discusses the results with corresponding figures and descriptions, while the second presents the conclusions. This study aims to understand As diffusion in Ge within the MOVPE process, considering the complex interplay of parameters. The knowledge gained also supports the development of Ge SJSC for TPV applications at IES-UPM, leveraging Ge's capability to absorb IR radiation, yielding promising outcomes [136], [189]. This dual focus leads to a thorough exploration of the MOVPE process for Ge TPV devices.

Figure 5.5. Target structure for Ge SJSC at IES-UPM.



The target Ge SJSC, illustrated in Figure 5.5, comprises an initial p-type Ge substrate, onto which a 50-nm GaAs nucleation layer is subsequently deposited. As the investigation will

show, the emitter emerges during an intermediate stage of GaAs deposition, facilitated by arsenic diffusion, culminating in the formation of the n-type region and the concomitant creation of the np junction. Following the nucleation layer, a 250-nm GaInAs contact layer is grown. This progressive approach enables a nuanced exploration of As diffusion into Ge through MOVPE processes, unfolding in different stages.

Figure 5.6 provides a schematic profile detailing the temperature evolution during the MOVPE growth stages, encompassing five different phases as previously mentioned. In the initial stage (stage 1), the p-type Ge substrate bears surface oxides. As the temperature surpasses 560 °C, the oxides desorb, and As from the reactor chamber dimerizes on the Ge surface, as seen from the measured RAS signatures [190]. Subsequently, the process involves a gradual temperature ramp-up and stabilization at 640 °C during the bake phase (stage 2), maintaining the Ge wafer at this temperature for 5 minutes to eliminate Ge oxides and ensure desorption of any foreign adsorbed elements. The introduction of AsH₃ into the reactor begins the formation of a monolayer of As on the Ge surface (stage 3), which stabilizes the surface [191] and displaces previous atoms from the Ge surface originating from the reactor wall. However, this also triggers As diffusion into Ge and causes surface roughening. In stage 4, GaAs deposition starts with TMGa flowing into the reactor, leading to cross diffusion of As and Ga between GaAs and Ge, and vice versa, occurring across the GaAs/Ge interface. Throughout this process, all elements continuously diffuse due to the thermal load. While the cross-diffusion involves multiple atoms (Ga, Ge, As, and Si as an n-type dopant in GaAs), this study primarily focuses on analyzing As diffusion. The influence of Ga is indirectly observed in the ECV profiles, as discussed later. In the final step, GaAs layer deposition concludes, and the heater is turned off to initiate the cooldown stage (stage 5). To prevent surface damage related to As desorption, a small AsH₃ flow is maintained down to 300 °C [192] during the cooldown process, which remains constant across all samples studied in this work.

The experimental data in this research pertains to samples grown on (100) Ge wafers with a 6° offcut towards the nearest (111) plane, featuring low dopings of Ga (p-type with a resistivity of 1.5-4.5 Ohm·cm). The precursors employed were high-purity AsH₃ and TMGa. The molar flows during growth were maintained at $4.4 \cdot 10^{-5}$ mol/min and $2 \cdot 10^{-2}$ mol/min for TMGa and AsH₃, respectively. Throughout the cool-down phase (see Figure 5.6), the molar flow of AsH₃ was held at $2.2 \cdot 10^{-3}$ mol/min to prevent As desorption until reaching 300 °C. DTBSi was introduced for n-type doping of the GaAs layer with Si. High-purity H₂ served as the carrier gas, with a constant growth temperature of 640 °C and a growth rate of 0.75 µm/h maintained for each sample.

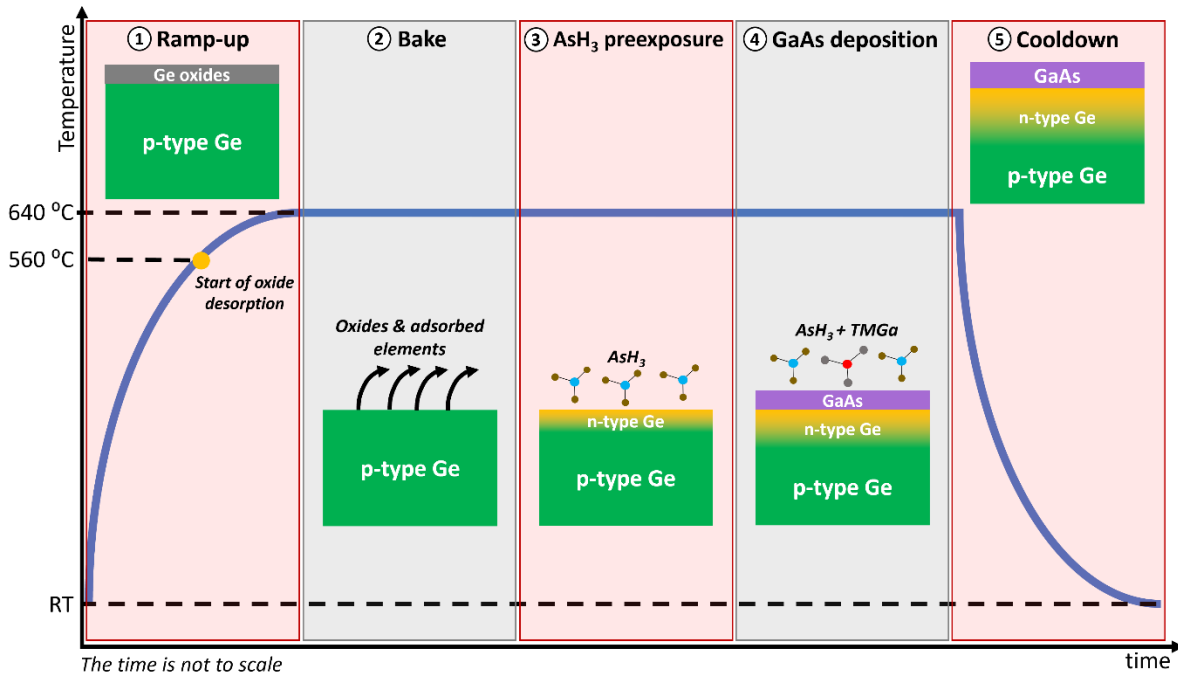


Figure 5.6. Schematic graph of the temperature profile in a GaAs deposition on Ge depicting the five stages of the process. Simplified illustrations of every stage are pictured. The time axis is not to scale.

This study focuses on researching the impact of three relevant stages, namely, AsH₃ preexposure, GaAs deposition and cooldown (stages 3, 4 and 5 in Figure 5.6), on As diffusion during MOVPE GaAs/Ge heteroepitaxy. These stages are pivotal in the overall process, encompassing substrate preparation and the subsequent growth phase. The decision to examine these specific stages is guided by their importance. The forthcoming chapters will provide additional details on the selection of these stages, as well as the results obtained from them.

5.4.1 Impact of AsH₃ preexposure

The need for analyzing the preexposure step arises from the intricate nature of heteroepitaxial growth, specifically in the context of depositing a GaAs layer on a Ge substrate. This process involves the growth of a polar semiconductor (GaAs) on a non-polar substrate (Ge), which introduces defects such as the appearance of APD [193]. Minimizing anti-phase disorder becomes critical, and one effective strategy is to promote GaAs growth on a Ge surface featuring As dimers with a single orientation and double steps [194]. The preexposure step is designed to achieve such a favorable surface condition by subjecting the wafer to the group-V precursor for a brief duration before the actual growth start [195]. The optimization of this preexposure step depends upon several factors, including reactor configuration, precursor partial pressure, and growth temperature, with timeframes shorter than a minute.

5.4.1.1 Morphological characterization

This section is dedicated to the characterization of surface morphology, driven by the observation that Ge substrates exposed to an AsH_3 environment at elevated temperatures can undergo etching [196], thereby altering their surface characteristics. To systematically assess surface roughening and its correlation with different As diffusion behaviors, a series of samples was prepared. Ge substrates underwent a t_{Preexp} variation ranging from 1 s to 20 s, followed by the deposition of 4-5 nm GaAs layers. This step was crucial for preventing oxide formation on the Ge surface [197] while preserving as much as possible the inherent Ge surface roughness for subsequent analysis.

Surface degradation characterization was conducted through AFM measurements, employing various t_{Preexp} values (1 s, 3 s, 5 s, 10 s and 20 s) immediately before the deposition of the oxide-protection GaAs layer. To investigate localized degradation, AFM scans were performed in three different areas: $2 \times 2 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$ and $10 \times 10 \mu\text{m}^2$. Representative images of each sample are presented in Figure 5.8. A visual trend is observed: with prolonged t_{Preexp} , the color tends to become brighter, indicating higher roughness. The RMS roughness was calculated and averaged from the acquired AFM images. The corresponding values are depicted in Figure 5.7, confirming the suspected trend of increasing roughness with an increase in t_{Preexp} .

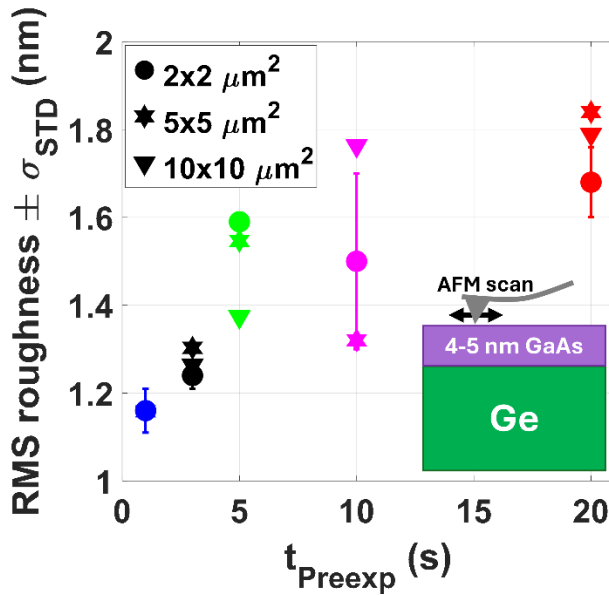


Figure 5.7. RMS roughness vs preexposure times. The RMS roughness obtained from different AFM scan areas is included (see Figure 5.8). The RMS values for $2 \times 2 \mu\text{m}^2$ areas include standard deviation (σ_{STD} ; represented by bars) whilst $5 \times 5 \mu\text{m}^2$ and $10 \times 10 \mu\text{m}^2$ scans were measured once.

Returning to Figure 5.8, the right column presents $5 \times 5 \mu\text{m}^2$ AFM images, with one-dimensional profiles of the surfaces in the left column derived from the corresponding AFM images. In these profiles, the arithmetic mean roughness falls within the range of 4-6 nm. By fixing this parameter affixed, it is observed that the peak-to-peak average increases with

prolonged t_{preexp} , confirming both the visual brightness analysis and the increase of RMS roughness highlighted in Figure 5.7.

5.4.1.2 Doping profile measurements

In the following series of experiments, Ge substrates underwent an increase in t_{preexp} durations before the epitaxial deposition of 50-nm GaAs layers for 240 s on each sample. The ECV profiles of this experimental set are presented in Figure 5.9. The initial dips within the first nanometers (up to approximately 25 nm) are attributed to the presence of Ga, acting as a p-type dopant that partly compensates for the n-type doping resulting from the pre-diffused As. Due to its lower diffusion coefficient compared to As, Ga's diffusion is significantly shallower. Following this dip, a plateau emerges in the electron concentration profile, eventually decreasing at a certain depth into the Ge wafer. Notably, the free carrier concentration corresponding to these plateaus diminishes with increasing t_{preexp} , while the profile depth increases. Thus, the main conclusion from Figure 5.9. is that four MOVPE processes conducted at the same temperature (640 °C) for comparable durations — ranging from 241 s in the black curve to 260 s in the magenta curve — yield remarkably different diffusion profiles.

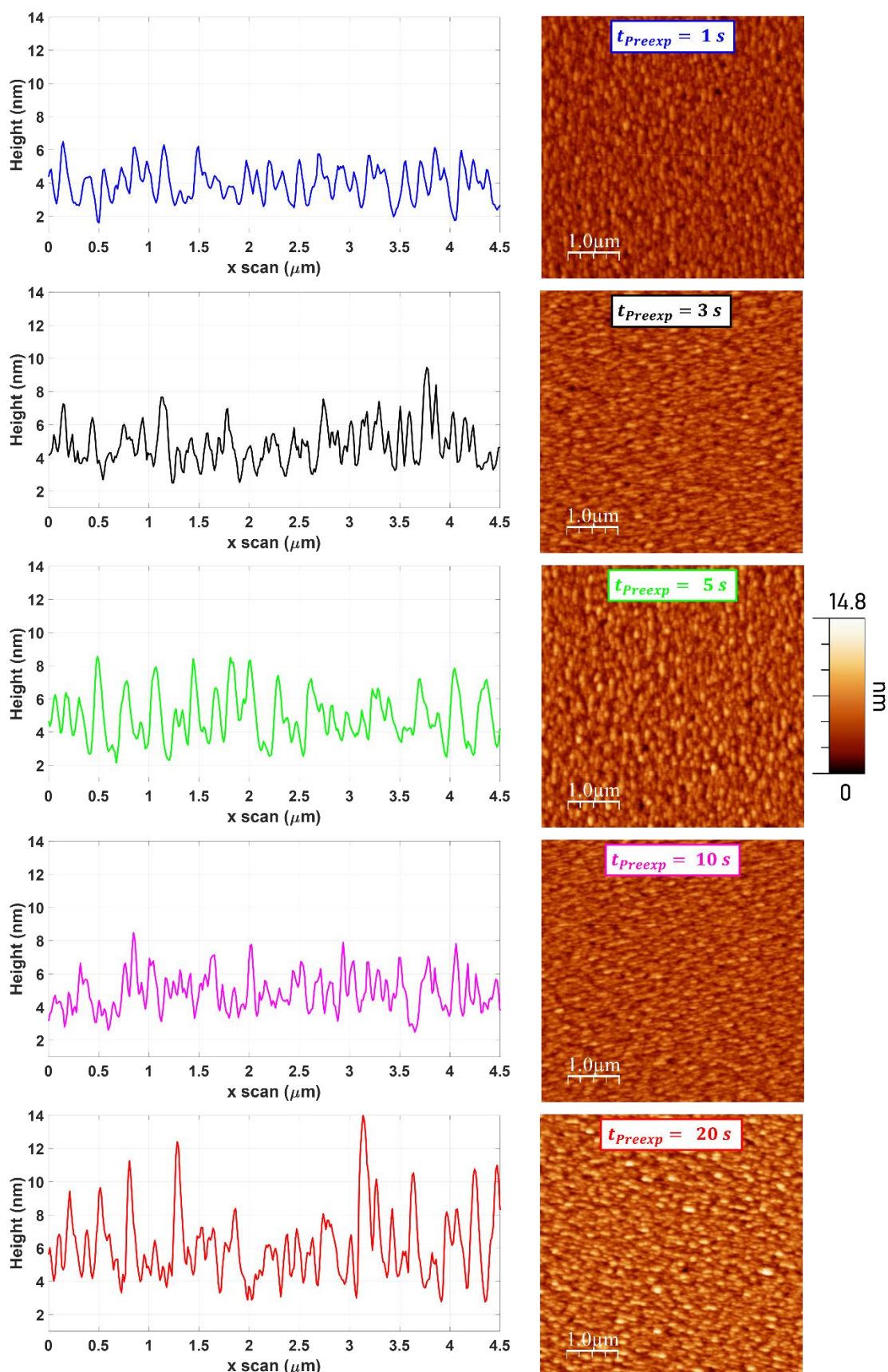


Figure 5.8. In the right column, AFM images of 5x5 μm^2 for each preexposure time, while the left column showcases one-dimensional profiles of the surfaces derived from the corresponding AFM images.

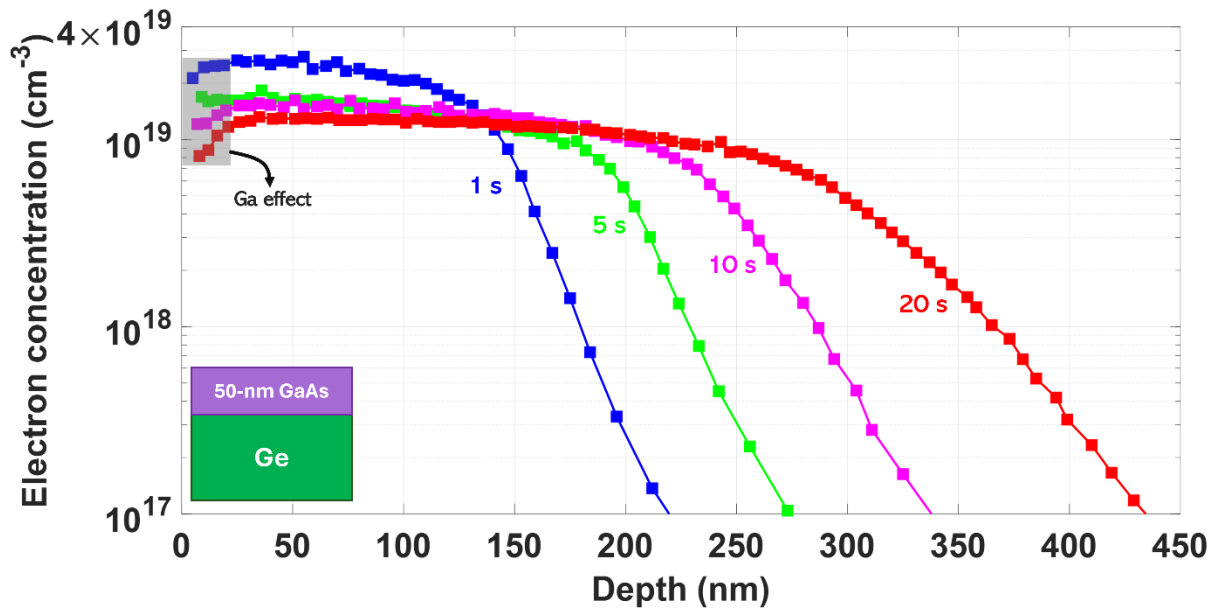


Figure 5.9. ECV profiles for the samples with 50-nm GaAs and variable AsH_3 preexposure times (colored numbers). A simple illustration of the structure is placed in the lower left corner. The shaded region in black tags the p-type influence exerted by Ga on the prevailing n-type profile.

The impact of the AsH_3 preexposure stage is evident in these experiments. To explore this influence, comprehensive analyses, considering both ECV and SIMS profiles, were conducted exclusively on samples subjected to this specific stage. As depicted in Figure 5.10, the ECV and SIMS profiles exhibit different characteristics in concentration plateaus. It is crucial to note that while SIMS counts the chemical profile, ECV profiles are sensitive to the effects of p-type elements (such as punctual defects). Consequently, the SIMS curves present higher concentrations. Two key observations emerge: firstly, at all depths of each measurement, the concentration levels are around 130-150 nm at 10^{17} cm^{-3} ; and secondly, the profiles exhibit similarity. Any subtle discrepancies in the profile shapes within the drop-off region can be attributed to the inherent variability in the MOVPE process for both cases. Additionally, for ECV profiles, uncertainties arise from the sensitivity of ECV electrochemical etching to surface roughness and other parameters that are challenging to distinguish without an in-depth analysis of the ECV equipment. Nevertheless, these discrepancies fall within the expected range for such measurements. Finally, it is important to note that SIMS measurements cannot easily differentiate between ^{75}As and $^{74}\text{Ge}^1\text{H}$. Consequently, the SIMS profiles show a background signal, approximately $2 \cdot 10^{17} \text{ cm}^{-3}$, because of this constraint. From now on, readers should keep this limitation in mind for future SIMS analyses.

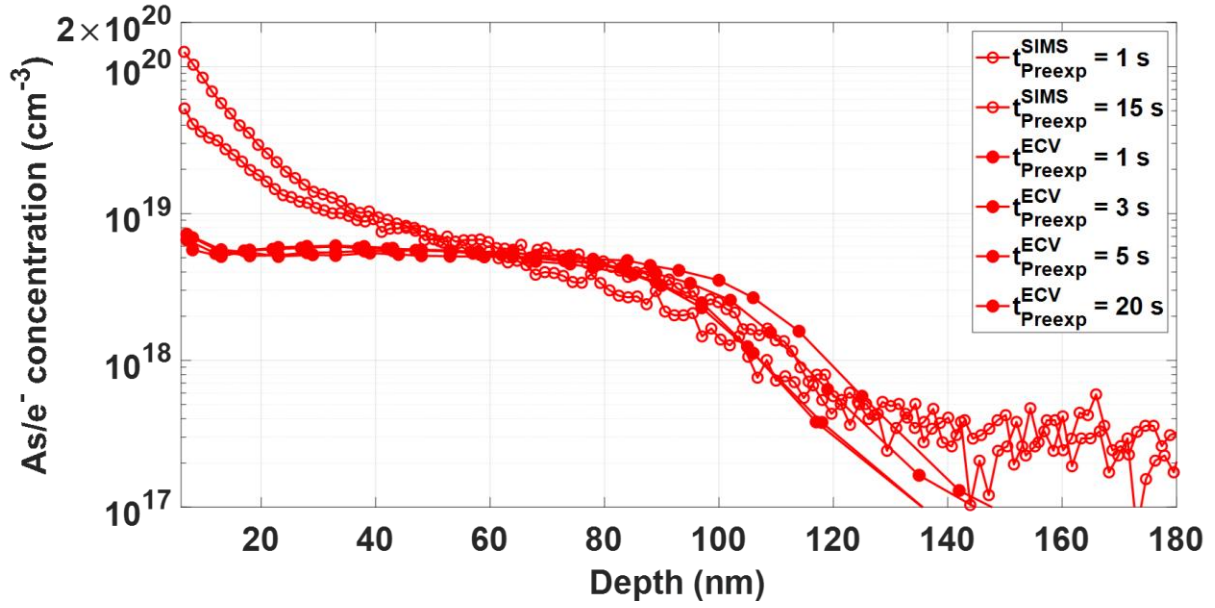


Figure 5.10. Concentration profiles obtained from SIMS measurements (empty circles) and ECV profiles (filled circles) for samples exclusively exposed to AsH_3 . The y-axis denotes the arsenic concentration, labeled as As, aligning with SIMS measurements, while the electron concentration from ECV measurements is denoted as e^- .

5.4.1.2.1 SIMS profile simulations

We investigate here the As SIMS profiles obtained through numerical simulation. Many studies in the literature have extensively explored group V diffusion in Ge [162], [164]. Ion implantation, a widely employed method for Ge doping in semiconductor applications, has been a focal point for investigating group V diffusion in Ge [198], [199], [200], [201]. Across these studies, a pattern emerges, highlighting a quadratic dependence on concentration, attributed to doubly negative charged vacancies. However, such a dependence is not universally applicable to other growth methods. In the context of MOVPE processes, different concentration dependencies have been observed, such as in [180]. This research explores various crystallographic directions ([100], [110], and [111]) of Ge wafers exposed to a tributylarsine (TBAs) environment at elevated temperatures. For (100) substrates under these conditions, arsenic diffusion exhibits a linear dependence, with corresponding values of $D_0 = 6.2 \cdot 10^{-3} \text{ cm}^2/\text{s}$ and $E_a = 1.9 \text{ eV}$ (Table V.II). It is essential to note that D_0 and E_a carry the same physical significance as indicated by Eq. 5.1, featuring a linear dependence on n , as described in Eq. 5.5 for $m=1$. Furthermore, in this simulation and subsequent ones, we assume that each incoming atom functions as an active dopant ($n = U$). It's important to note that the simulations in this chapter and the following ones follow this approach.

In our case, the preexposure (stage 3 in Figure 5.6) is performed under similar conditions, except for the precursor, specifically AsH_3 in this case. Additionally, the orientation of the used

wafers coincides with [100], enhancing the applicability of this model. Two crucial parameters for comparison are the aforementioned D_0 and the value of the infinite source (U_0), as E_a remains constant. In the reference study [180], U_0 is estimated to be approximately 10^{19} cm^{-3} . Our present simulation adopts the same boundary condition due to the abundant presence of arsenic dimers on the Ge surface [191] and the continuous high flow of AsH_3 at 450 sccm during t_{preexp} . Considering these parameters, the comparison between simulations and SIMS profiles is presented in Figure 5.11, where the shape of the experimental profiles suggests the potential validity of linear diffusivity, as it closely resembles the red profile in Figure 5.2.

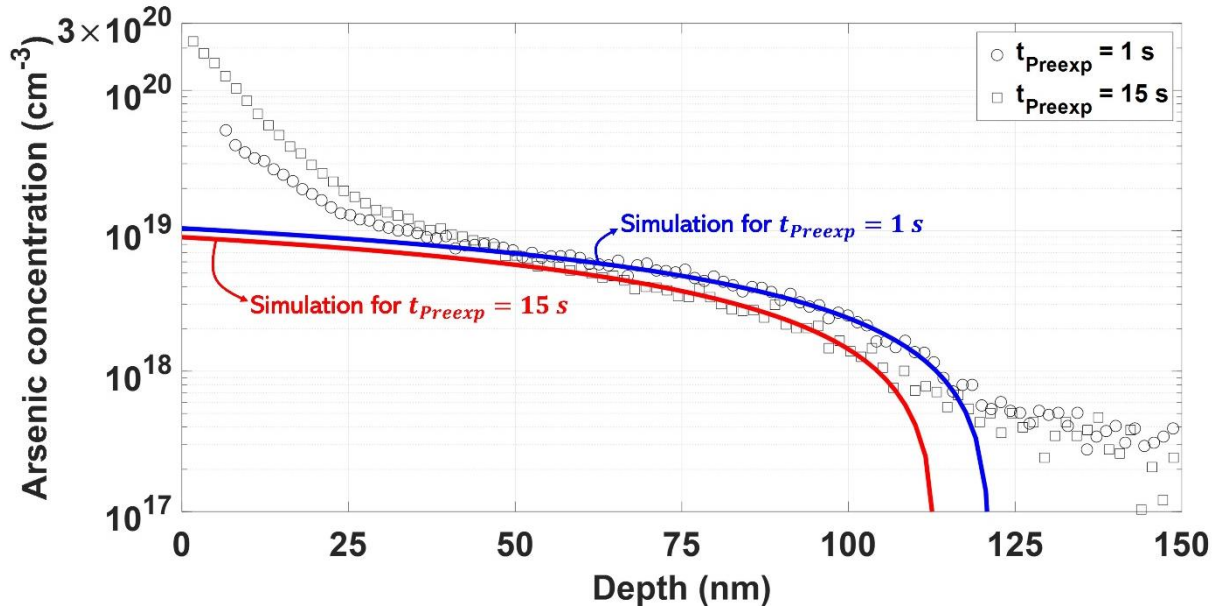


Figure 5.11. SIMS profiles for samples with AsH_3 preexposure times of 1 s (black circles) and 15 s (black squares). Simulations, depicting a linear concentration dependence, are overlaid on the experimental data. The blue line corresponds to the simulation for the 1-s profile, while the red line represents the 15-s profile simulation.

As a first approach, the simulations take a conservative approach by not accounting for potential effects caused by the accumulated arsenic within the first nanometers. Consequently, any values surpassing the threshold of U_0 are disregarded in the analysis. This conservative stance ensures that the simulations capture the diffusion dynamics accurately without being influenced by the localized buildup of arsenic at the surface. By excluding these initial accumulations from consideration, the simulations focus on the deeper diffusion behavior of arsenic atoms, providing insights into their penetration depths and distribution within the material. This practical approach helps clarify the diffusion process without adding unnecessary complexity or bias to the model. In addition, the simulation code incorporates the variation of the bandgap and the intrinsic carrier concentration with temperature [202], ensuring that the temperature profile accounts for the cooling phase as well (stage 5 in Figure

5.6). Observably, the SIMS profiles, particularly in the drop-off region, mirror the linear-dependent profile outlined in Figure 5.2, reinforcing the hypothesis of a diffusivity with this concentration dependence. The simulation values of U_0 and D_0 , along with values from [180], are tabulated in Table V.III. For convenience, the relative error for diffusion coefficients is provided, showcasing close proximity to the values in [180], considering the relative errors shown in Tables IV.I and IV.II, which hover around 40%-50% in the worst cases. In diffusion studies, these differences are deemed reasonable due to the variability in experimental conditions among similar research and inherent measurement variability. Regarding U_0 , the acceptable differences between our simulations and the literature are considered, acknowledging the discussed variability in any MOVPE process.

	Reference [180]	$t_{\text{Preexp}} = 1 \text{ s}$	$t_{\text{Preexp}} = 15 \text{ s}$
$D_0 (10^{-3} \text{ cm}^2/\text{s})$	6.2	6.3	5.5
$\epsilon_{\text{rel}}^{D_0} (\%)$	-	2	11.3
$U_0 (\text{cm}^{-3})$	10^{19}	$1.05 \cdot 10^{19}$	$9 \cdot 10^{18}$

Table V.III. tabulated values of D_0 and U_0 for As diffusion simulations, comparing results from the reference literature with profiles obtained after AsH_3 preexposure times of 1 s and 15 s. Relative errors ($\epsilon_{\text{rel}}^{D_0}$) are provided for comparisons with the reference value of D_0 .

5.4.2 Effects of GaAs deposition following AsH_3 preexposure

As illustrated in Figure 5.6, following the preexposure, a subsequent GaAs deposition is carried out. The start of GaAs layer growth initiates the cross-diffusion, as elaborated in Section 5.3. The extent of atomic interchange at the GaAs/Ge interface during this process may vary based on the surface roughness of Ge. Moreover, the cross-diffusion across the GaAs/Ge interface inherently alters the thermodynamics of the experiment. Receiving As atoms from a gas phase may exhibit differences from receiving them from a solid source like GaAs. This raises suspicions about potential shifts in the diffusion dynamics. To explore this aspect, the established model is used to simulate arsenic diffusion, including the deposition of GaAs, to support future analyses. It is important to note that each sample presented follows the temperature profile detailed in Figure 5.6.

5.4.2.1 Doping profile measurements

The experimental design encompassed two growth scenarios: (I) Samples featuring constant t_{Preexp} and varying t_{GaAs} , and (II) samples with identical GaAs deposition time but varying durations of t_{Preexp} . In Figure 5.12, a series of scenario I is presented. In addition to the samples with AsH_3 preexposure and GaAs deposition, the profile for the 15-s sample under

only AsH_3 is included to provide a direct track of the evolution. Unfortunately, the 20-s sample under only AsH_3 was damaged, preventing measurements. Nevertheless, it still holds value for tracking purposes. All profiles showcase an abrupt high concentration until approximately 50 nm, after which plateau concentrations gradually decline before ultimately decreasing at some depth into the Ge. Noticeably, there is an increase in diffusion depths as the thickness of GaAs grows. It is important to underscore that extended deposition times lead to higher As doses, a correlation supported by the larger areas under the profiles. This finding provides compelling evidence for the continuous diffusion of As atoms into Ge during the GaAs deposition phase.

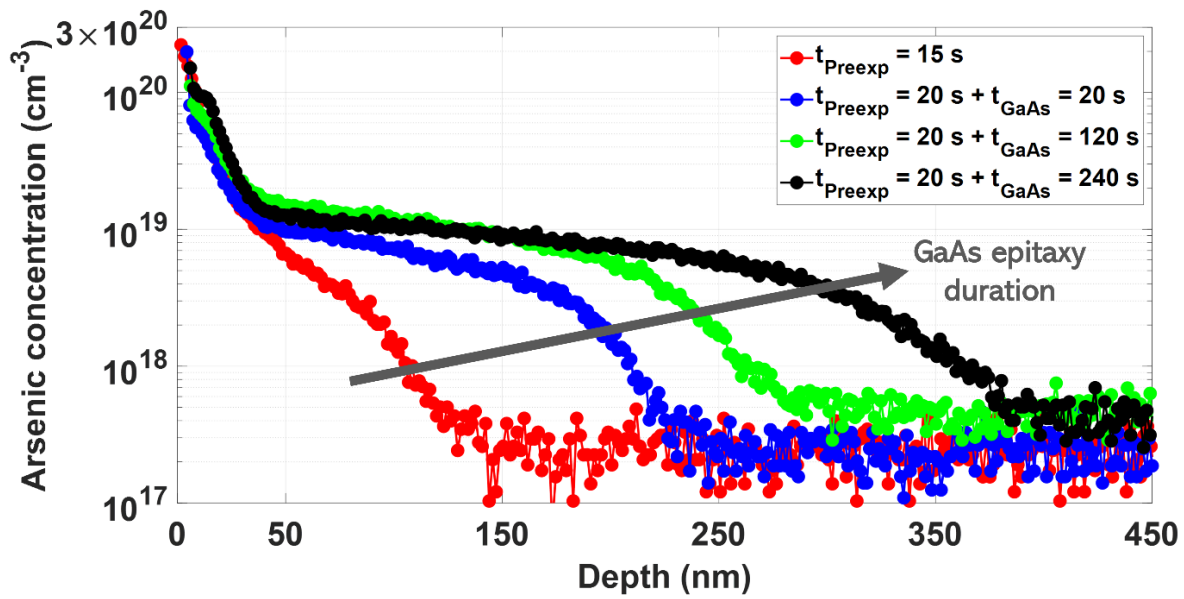


Figure 5.12. SIMS profiles illustrating As distribution in samples with varying GaAs thicknesses and a consistent preexposure time of 20 seconds. Profiles corresponding to GaAs deposition times of $t_{\text{GaAs}} = 20$ s (blue), $t_{\text{GaAs}} = 120$ s (green), and $t_{\text{GaAs}} = 240$ s (black) are depicted. Additionally, a sample subjected solely to AsH_3 preexposure for 15 seconds (red) is included to directly observe the evolution of As diffusion.

Concerning scenario II, Figure 5.13 compares the SIMS profile of a preexposure-only experiment with a pair of profiles with constant t_{GaAs} of 20 s and different t_{Preexp} . Upon analysis, the SIMS profiles, in conjunction with GaAs deposition, align with the ECV profiles in Figure 5.9. The main question here is: if a brief AsH_3 preexposure stage fails to differentiate As depths, what mechanism underlies profiles with the same t_{GaAs} exhibiting disparate depths? This prompts an exploration of the potential influence of GaAs deposition on As diffusion.

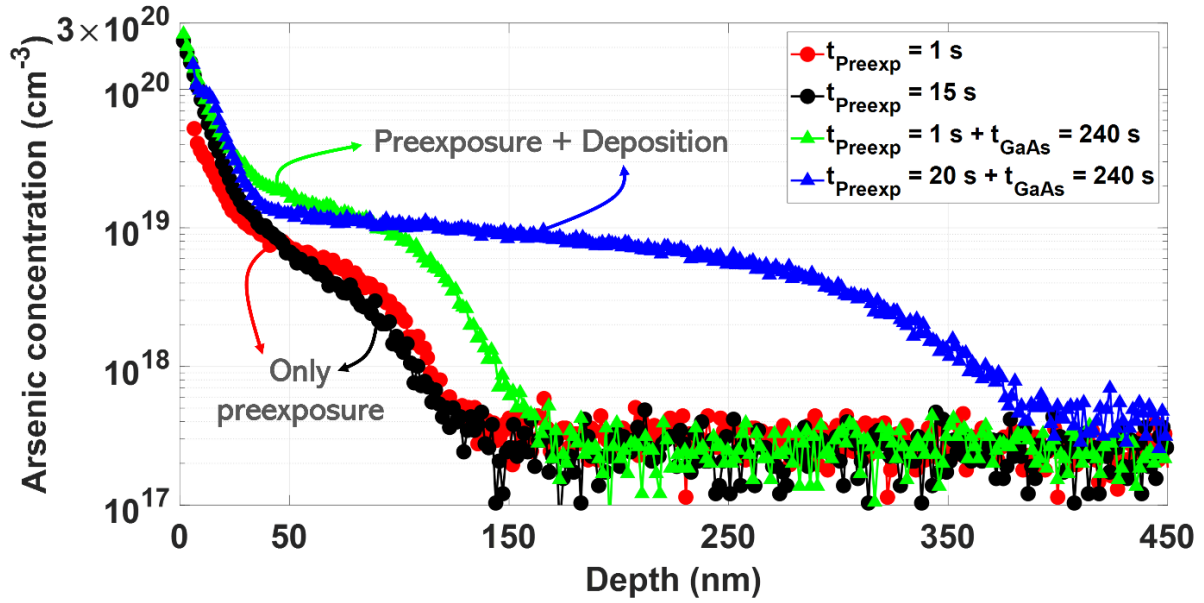


Figure 5.13. Profiles of As determined by SIMS for various growth conditions. Filled circles represent profiles of samples exposed to AsH_3 for 1 s (red) and 15 s (red). Upward triangles indicate samples with $t_{\text{GaAs}} = 240$ s, with different preexposure times of 1 s (green) and 20 s (blue).

5.4.2.1.1 SIMS profile simulations

Figure 5.14 illustrates the SIMS profiles of different samples: one subjected only to preexposure to AsH_3 (black squares), another with a comparable preexposure followed by a brief GaAs growth (red circles), and the associated simulations (blue lines). The blue solid line corresponds to the simulation of the sample with solely AsH_3 preexposure, with fitting values detailed in Table V.III for the 15-second sample. To replicate the evolution of the sample with preexposure and GaAs growth (red circles), the same model was applied, with an extension of diffusion time by 20 seconds (equivalent to the GaAs growth time), resulting in the profile depicted by the blue dashed line. However, the actual diffusion during these additional seconds (indicated by red circles) results in As penetrating to much greater depths. This means that the deeper diffusion profile of the sample with GaAs cannot be explained solely by the longer thermal load caused by the growth of this layer. To align with the experimental SIMS profile, utilizing the previous model (with the same U_0 and D_0), the necessary time to match the blue curve would be 15 times longer (blue dotted line). In essence, for an accurate representation of the As diffusion process in a MOVPE ambient, it is important to note that GaAs deposition significantly amplifies the diffusivity of As.

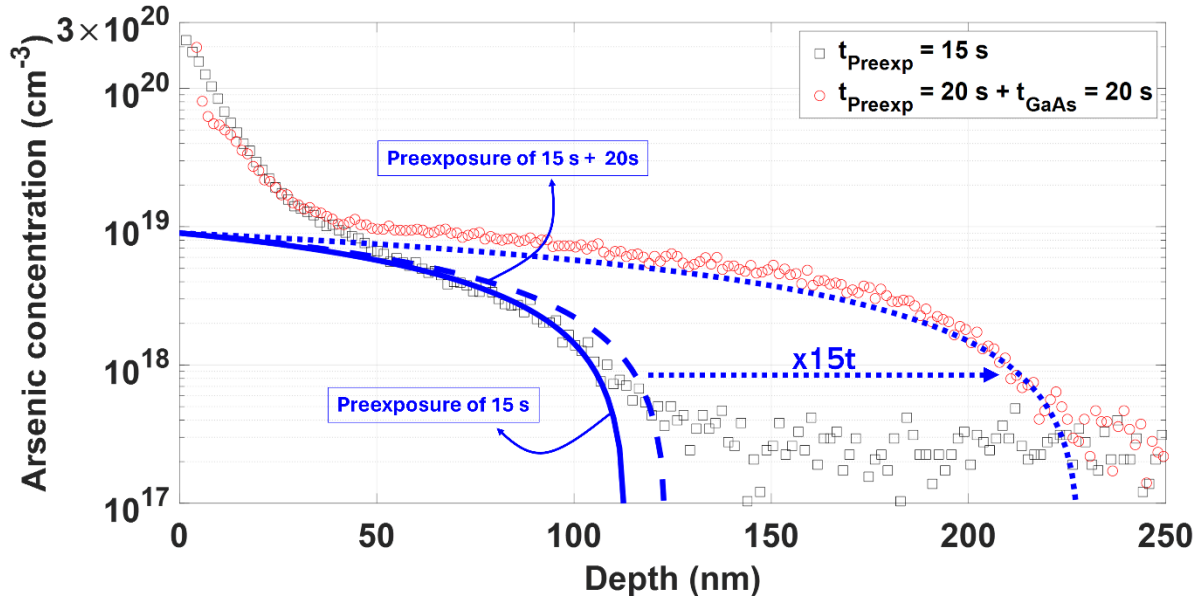


Figure 5.14. SIMS profiles depicted with black and red markers alongside simulated profiles using a linear dependence in concentration (blue lines). The blue solid line corresponds to the simulation based on the experimental data for the sample exposed to AsH_3 for 15 seconds (black squares). Additionally, a profile with an extra 20 seconds (blue dashed line) beyond the blue solid profile is presented. The blue dotted line illustrates another simulated profile, requiring approximately 15 times the duration (from the blue dashed profile) to match with the red profile.

Following the proof of enhanced diffusion due to GaAs deposition, an exploration into simulations has been undertaken for samples with extended t_{GaAs} . In Figure 5.15, simulations were performed for samples with varying t_{GaAs} while maintaining a constant t_{Preexp} of 20 s. The simulation of diffusion profiles involves three phases. The first phase is preexposure, representing the initial stage simulated using the parameters from Figure 5.14, depicted by the blue solid curve, and constant across all samples. The second phase is growth, which is a step with varying durations depending on the sample. The third and final phase is cooldown, characterized by a gradual temperature decrease while As diffusion persists, and this stage is the same for all samples. The colored thick lines in Figure 5.15 depict the profiles calculated using this approach, which show an excellent fit to the experimental data. Achieving these accurate fits needs maintaining the average pre-exponential diffusivity factor (D_0) almost constant, with a value akin to that observed in the simulation of preexposure-only samples (see Figure 5.11). Additionally, there is an average increase of approximately 150% in U_0 compared to the literature reference. While specific parameter values are not emphasized given the simplicity of the diffusion model, our assertion is that employing the same model as in Figure 5.14 yields reasonable fits for samples with extended GaAs growth. This quantitative support underscores the enhancing role of GaAs epitaxial growth.

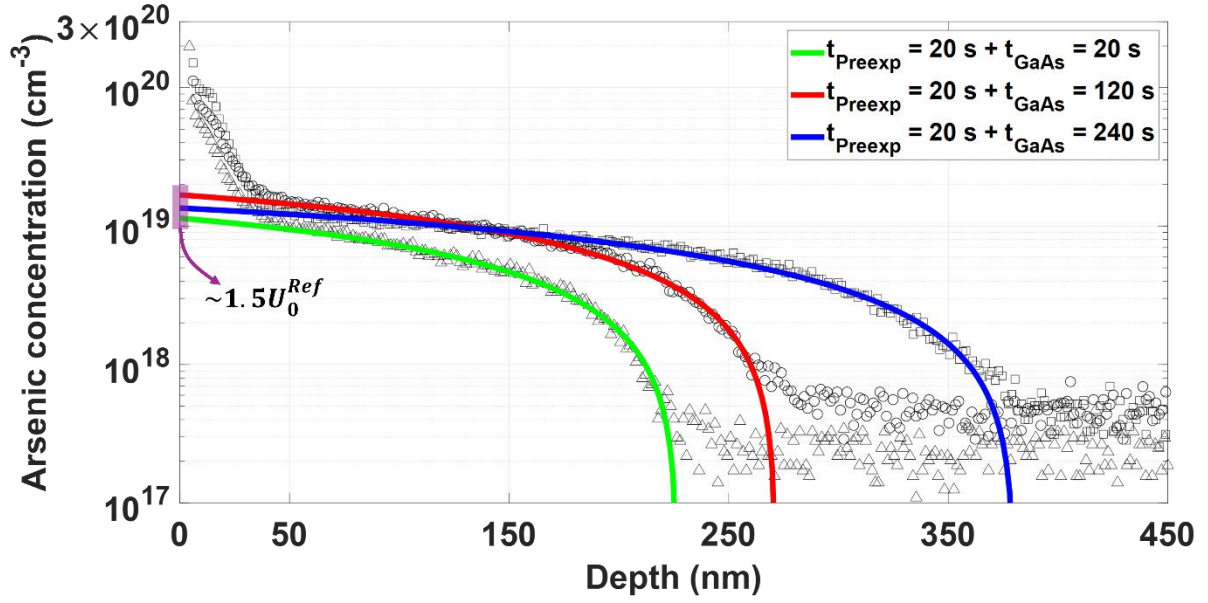


Figure 5.15. SIMS profiles depicting samples with a constant AsH_3 preexposure time of 20 seconds and varying GaAs deposition durations. The purple shaded area denotes that the boundary conditions for simulation are, on average, 1.5 times higher than the reference value U_0^{Ref} [180].

5.4.3 Cooldown influence on GaAs/Ge MOVPE growths

Based on the simulation results and the specified conditions, As diffusion ceases to be significant at temperatures slightly above 500 °C. This cooling period of 5 minutes, which exceeds the longest t_{GaAs} (4 minutes required for 50 nm of GaAs deposition), introduces an additional thermal load, facilitating the continued diffusion of As to greater depths. Additionally, a consistent AsH_3 flow is used in all samples during cooldown.

We now focus on the role of the cooldown step on the As profiles obtained. In Figure 5.16 we show the As SIMS profiles under different diffusion scenarios, the fit to these experimental data, and the calculated profiles using the fitting parameters but removing the effect of the cooldown step. A significant effect of the cooldown stage is observed in all cases. This effect is more pronounced in samples with shorter growth times, since the cooldown represents a larger fraction of the total thermal load.

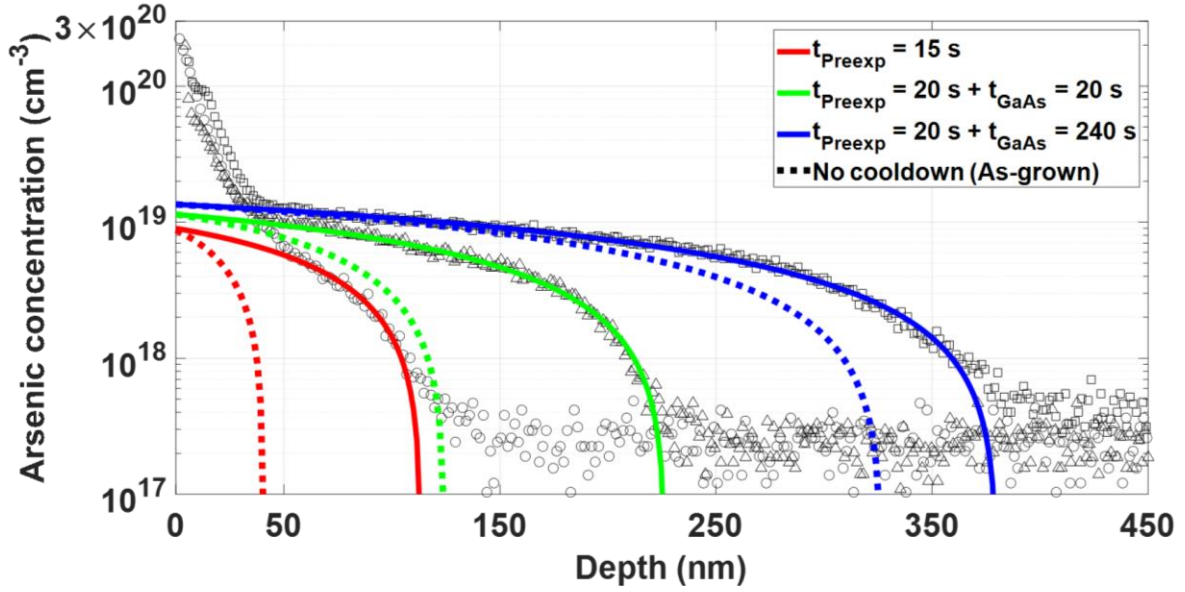


Figure 5.16. SIMS profiles illustrating the diffusion characteristics of samples subjected to various treatments: (1) AsH_3 preexposure for 15 seconds (black circles), (2) 20 seconds of preexposure followed by 20 seconds of GaAs deposition (black triangles), and (3) 20 seconds of preexposure followed by 240 seconds of GaAs deposition (black squares). The colored solid lines depict simulations based on linearly dependent diffusivity in concentration. Dotted lines indicate the profiles right before the initiation of the cooldown stage (As-grown).

5.5 Discussion and conclusions

In this final section, we synthesize the findings from the preceding discussions, encompassing simulations, measurements, and comparative analyses.

- Impact of AsH_3 preexposure:** The presented model of linearly concentration-dependent arsenic diffusion effectively captures observed phenomena. Under typical preexposure durations (1 to 20 seconds) of Ge to AsH_3 in MOVPE conditions, the resulting arsenic profile remains shallow and consistent across samples, aligning with findings reported using TBAs [180]. Significant chemical interactions occur between AsH_3 (and its byproducts) and the Ge surface at process temperatures, as evidenced by AFM measurements revealing surface morphology changes (refer to Figure 5.8). Prolonged exposure to AsH_3 leads to increased surface roughness, attributed to Ge hydration and subsequent dimer displacement [203]. This phenomenon induces etching of the Ge wafer, resulting in the removal of Ge atoms from the surface and creating a driving force for bulk Ge atoms to diffuse towards the surface to restore thermodynamic equilibrium. This process predominantly generates vacancies in the subregion adjacent to the surface, with

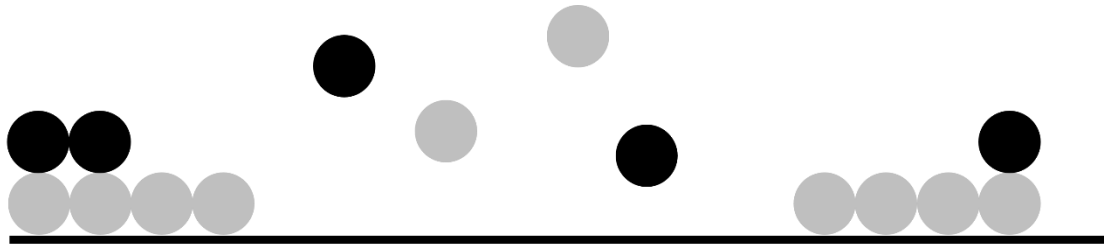
displaced Ge likely forming germane and desorbing into the gas phase. Essentially, the AsH₃ preexposure phase facilitates vacancy injection, a mechanism reminiscent of phosphorus diffusion into Si in MOVPE conditions using PH₃ as a precursor [204].

The influence of vacancy injection on diffusion dynamics is clear in both Figure 5.11 and Figure 5.13, with particular focus given to the latter due to its broader array of profiles. Examination of Figure 5.13 reveals a pronounced association between the duration of AsH₃ preexposure and the resulting diffusion profile post-GaAs deposition. Notably, despite similar process conditions—comprising identical temperatures (640 °C) and comparable process durations—the observed diffusion profiles exhibit substantial discrepancies. For instance, the profile generated from a mere 1-second AsH₃ preexposure followed by 240 seconds of GaAs growth contrasts with that resulting from a 20-second preexposure and an identical GaAs growth duration. Surprisingly, the marginal 19-second disparity in total process time (~5%) fails to account for the pronounced divergence between these profiles. Moreover, while initial free electron concentrations (n) could contribute to such variations, Figure 5.13 shows negligible differences in As concentration at the onset of diffusion, despite varying preexposure times. In essence, neither variations in diffusion temperature, process duration, nor initial As concentration substantially differ among the experiments showcased in Figure 5.11. Consequently, the concentration of vacancies within the Ge subsurface emerges as the pivotal factor driving the observed disparities in diffusion profiles, underscoring the subtle interplay between vacancies and diffusion parameters.

- **Effects of GaAs deposition following AsH₃ preexposure:** In Figure 5.15 simulations reveal an accelerated diffusion of As during GaAs growth. Prior studies have often associated enhanced dopant diffusion in Ge, as well as in Si, with the generation of additional point defects, notably vacancies in saturated regions [204]. The process of injecting vacancies into the Ge wafer during GaAs growth occurs as the GaAs epilayer draws in Ge atoms, leaving vacancies behind. At a given temperature, factors limiting cross-diffusion include the crystal orientation of the GaAs/Ge interface and the quality of the GaAs layer. As GaAs

growth begins, etching halts as AsH_3 is no longer in contact with Ge, freezing the surface morphology. With brief preexposure, minimal etching occurs, resulting in a GaAs/Ge heterointerface that closely follows the nominal wafer orientation, promoting optimal epitaxy and crystalline quality of the epilayer. Conversely, prolonged preexposure leads to surface roughening, potentially introducing higher index crystal planes and a correspondingly rougher GaAs/Ge heterointerface. Experimental observations in Figures 5.14 and 5.16 support these points, suggesting that the dissimilar profiles are likely a result of a combination of preexposure-induced surface degradation and cross-diffusion phenomena.

- **Cooldown influence on GaAs/Ge MOVPE growths:** Figure 5.16 visually portrays the significant influence of the cooldown stage on the overall process outcome. In our MOVPE procedure, this stage typically lasts approximately 5 minutes, as simulations indicate that diffusion halts once temperatures slightly above 500 °C are reached. Consequently, this phase extends beyond all preceding steps in the process and As diffusion continues until reaching this temperature threshold, resulting in penetration to greater depths. In addition to the aforementioned factors, it's crucial to highlight the significance of cooldown duration in terms of arsenic diffusion dynamics. When the cooldown period aligns closely with the duration of preceding processes, the extent of arsenic diffusion tends to be less pronounced.



Summary, conclusions and future works

CHAPTER 6

The collection and conversion of light into electricity are advancing towards the integration Ge and III-V materials to achieve superior efficiencies. This shift is largely driven by the approaching efficiency limits of Si, which are increasingly difficult to overcome due to inherent material constraints. The escalating demand for photovoltaic energy necessitates the exploration of more efficient materials and innovative designs, with Ge and III-V materials emerging as promising candidates.

Despite their potential, Ge and III-V materials are significantly more expensive than Si, primarily due to their lower abundance in the Earth's crust and the longer, more complex processes required to create complete III-V semiconductors. This economic challenge necessitates the development of alternative approaches that strike a balance between efficiency and cost. One viable strategy is the optimization of Ge usage, maximizing its utility with minimal material consumption. Additionally, leveraging the well-established Si-based industry by combining Si with Ge and III-V materials offers a pragmatic path forward. While Si may be nearing its theoretical maximum efficiency, its extensive use in the electronic industry underscores the importance of incorporating it into new hybrid systems. The combination of Ge and III-V materials with Si, however, is not straightforward and requires extensive research due to the complexities involved in their integration. These hybrid systems demand a thorough understanding of cross-diffusion processes, interface characteristics, and overall device architecture to realize their full potential.

To address these challenges, in-depth studies are essential to explore the synergistic effects of these materials. Such research efforts will be pivotal in optimizing light collection and energy conversion, ultimately providing a sustainable and cost-effective solution to meet the growing energy demands. By pursuing these innovative approaches, we aim to achieve a trade-off between high efficiency and economic viability, paving the way for the next generation of photovoltaic devices.

In this doctoral thesis, we focus on exploring innovative designs for III-V epitaxial deposition using alternative substrates. Specifically, we investigate two different approaches for future applications. The first approach involves utilizing an ultra-thin layer of Ge on Si to bridge the lattice mismatch between Si and common III-V materials. This method aims to facilitate the integration of III-V materials on a Si platform, thereby enhancing efficiency while aligning this new design more closely with the extensive infrastructure of the Si-based electronics. The second approach entails a specialized treatment of commercial Ge substrates. This treatment enables the detachment of the device after any deposition process, preserving sufficient Ge thickness for subsequent epitaxial growth. This technique not only optimizes the use of Ge but also allows for multiple reuse of the Ge substrate, significantly reducing material costs.

Achieving optimized efficiency in these hybrid systems necessitates a thorough understanding of every stage in the epitaxial deposition of III-V materials on Ge. A key aspect of this research is the study of group-V element diffusion, specifically arsenic, to optimize the formation of the np junction. The properties of this junction, particularly the emitter width, are crucial for the performance of the resulting devices. By comprehensively analyzing arsenic diffusion, we aim to refine the np junction creation process-

6.1 Summary and conclusions of the main research findings

Subsequently, the findings will be synthesized and detailed in the chapters that present the research results.

- **Ultra-thin Ge|Si virtual substrates** have shown potential in solar cell applications (Section 1.2.4.2). Nevertheless, a significant reduction in TDD is essential to achieve higher V_{oc} . Motivated by this requirement, a series of experiments were conducted to explore variations in deposition growth parameters (detailed in Tables III.I and III.II) using the RF-PECVD technique. The specific details of this method are elaborated in the last paragraph of Section 1.2.3.2 and in Section 2.1.1. However, the experimental results, as detailed in Chapter 3, presented a discouraging outlook, with the corresponding sections analyzing the research findings.

The high TDD, approximately $5 \cdot 10^9 \text{ cm}^{-2}$ or higher, poses a significant threat to the minority carrier lifetime and increases the saturation current density according to the diode model, if these samples were to be processed into complete solar devices. Additionally, the characterization of the virtual substrates and the subsequent III-V depositions revealed considerable inhomogeneity, precluding any conclusive analysis beyond identifying the presence of rough, low-quality surfaces and epitaxies. Moreover, no consistent trends were observed across different batches.

For instance, AFM images of samples within the same batch group (varying in thickness and growth temperature) do not exhibit a consistent trend. That is, the surface morphology and roughness remain dissimilar within the same group. Furthermore, RAS measurements for the T-batch group show virtually identical signals, indicating similar surface reconstruction. However, EBSD maps reveal a deformation distribution that does

not follow a consistent pattern within the same group. This discrepancy underscores the complex interplay of factors influencing the microstructural properties of these materials, which may not be immediately evident through surface analysis alone.

Despite the inherent challenges, the previous functionality of virtual substrates in photovoltaic cells highlights the critical need to minimize TDD, surface roughness, and non-uniformity. The achievement of reduced TDD, lower surface roughness, and enhanced uniformity is essential for progressing this technology as a viable and cost-effective alternative to conventional solar devices.

Current advancements in virtual substrates, specifically those produced using low-temperature LT-PECVD, have yet to demonstrate compatibility with the epitaxial growth of MJSC structures. These virtual substrates have not yet proven to achieve the requisite characteristics for optimal current extraction and efficiency. Thus, further research and development are necessary to enhance their performance to meet the demanding criteria required for high-efficiency solar applications.

- **Germanium-On-Nothing** substrates have demonstrated significant potential for use in MOVPE III-V deposition, as discussed in Chapter 4. RAS measurements confirmed the good surface quality of the GON substrates. The RAS signals from GON samples exhibited negligible differences in surface reconstruction compared to those from a standard Ge wafer, indicating that the surface properties of the GON substrates are comparable to traditional Ge substrates. This consistency suggests that the micropillars supporting the Ge foil are predominantly or entirely intact, as any substantial damage would have resulted in detectable deviations in the RAS measurements.

Electrical characterizations of TJSCs on GON substrates, when compared with identical TJSC structures on standard Ge substrates, revealed remarkable similarities in EQE and J-V curves, despite a marginal decrease in performance. Notably, substrates with the lowest

micropillar density showed clear degradation in both light and dark J-V curves, evidenced by a lower V_{oc} (approximately 0.3 V) and a higher ideality factor, indicating compromised device performance.

The mechanical properties of these alternative Ge substrates, specifically the micropillars supporting the Ge foil, have proven capable of withstanding the GaInP/GaInAs/Ge(foil) TJSC and the entire post-processing sequence, including critical steps such as lithography and metallization. Partial detachment of the solar device from these substrates was successfully achieved using Kapton tape. While some sections of the device remained adhered to the tape during the initial successful transfer, others were damaged during the second transfer attempt. Although the fully separated sections are currently insufficient for a fully functional device, these substrates exhibit promising potential for reusability applications, provided that the separation method is improved.

- The evaluation of **As diffusion into Ge during the MOVPE deposition of GaAs** has yielded notable insights into optimizing the formation of np junctions for advanced electronic devices. Detailed analysis of arsenic concentration profiles, obtained through SIMS and ECV measurements, has highlighted the sensitivity of As diffusion to minor variations in the MOVPE process, specifically the preexposure stage under AsH_3 prior to GaAs epitaxial growth.

The study found that, within the timeframe examined, the As diffusion profiles remained largely unchanged, with no significant variations detected in the SIMS and ECV profiles. However, the preexposure to AsH_3 thermodynamically modifies the Ge system, leading to the formation of Ge vacancies during this stage. Analysis of the As concentration profiles revealed two key observations: (I) a longer preexposure duration leads to deeper As penetration profiles, and (II) the formation of new Ge vacancies during the preexposure stage enhances As diffusion. These effects were observed following the GaAs deposition.

These findings were corroborated through numerical simulations. Conventionally, As diffusion is described by a quadratic dependence on electron concentration. However, our model, which adopts a linear dependence as previously reported by Takenaka et al. [1] in MOVPE environments, aligns more closely with our experimental data. This linear model accurately describes the enhanced As diffusion observed during the GaAs deposition phase. When applying the model to the As profiles post-GaAs deposition, it was found that the D_0 and U_0 (with E_a kept constant) increased, resulting in an excellent fit to the experimental data. This confirms that preexposure to AsH_3 modifies the Ge system by creating V_{Ge} , which facilitates increased As diffusion during GaAs deposition. It is important to note that this model is primarily utilized for qualitative description and refinements are necessary to achieve a more accurate and quantitative analysis.

Another significant finding is the sensitivity of the diffusion process to the MOVPE system configuration. During the cooldown stage, the temperature gradually decreases, which impacts the diffusion process as it continues until the temperature falls below the threshold where diffusion ceases. Analysis of the As profiles indicates that, as the deposition duration approaches the duration of the cooldown phase, the depth of the As profiles increases. Consequently, MOVPE systems with rapid cooldown rates may mitigate this issue, while those with slower cooldown rates should carefully account for this phase to achieve more accurate and reliable outcomes.

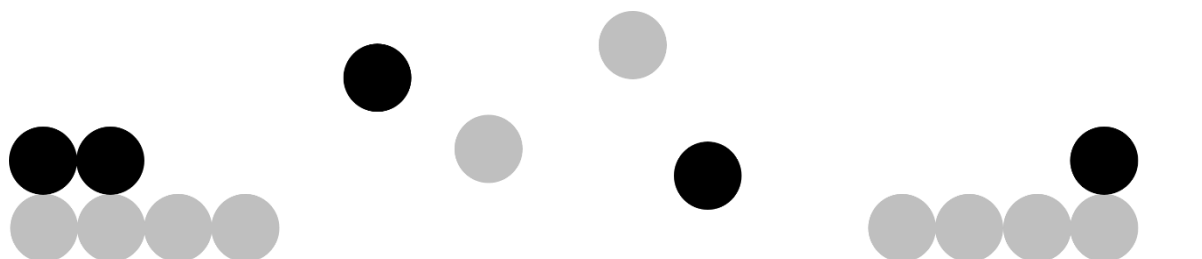
6.2 Future works

In line with the previous section, the following future research directions will be outlined individually, each corresponding to specific aspects of the study:

- **Improvement of Ge|Si Virtual Substrates:** The analysis of Ge|Si virtual substrates has highlighted substantial areas for improvement, particularly concerning the high TDD, significant RMS roughness, and non-uniform surface morphology and deformation distribution. These factors present considerable challenges for effective epitaxy. Despite previous demonstrations of MJSCs on these substrates, their performance was significantly hindered by the high density of TDs. To advance this area, it is crucial to develop substrates with improved quality. Alternative Ge|Si virtual substrates based on

thick Ge layers deposited by CVD show lower TDD but the risk of crack formation. Designs that prevent this, based on thinned MJSC structures, are under exploration.

- **Advancements in Germanium-On-Nothing Substrates:** GON substrates have demonstrated promising performance for the epitaxial deposition of TJSCs. Their effectiveness in PV applications is evident, but further work is required to address the challenges associated with substrate detachment. Refining the transfer process is essential for the practical application of these substrates in various solar devices. Once these issues are resolved, exploring additional epitaxial designs for III-V materials via MOVPE can be pursued, potentially expanding the scope of future research. An alternative to the GON technology under development is based on engineering standard Ge substrates by creating porous Ge layers with reconstructed epifoils. The absence of costly nanolithography steps makes this substrate engineering approach much more cost-effective, but the ability to create fully epi-ready and detachable Ge foils in the context of multijunction cells are yet to be demonstrated.
- **Refinement of As Diffusivity Models in Ge:** The strong correlation between As diffusivity and electron concentration in Ge presents opportunities for refining characterization methods and enhancing model accuracy. Future research should investigate the effects of diffusion near interfaces, particularly in dopant saturation regions, and employ characterization techniques such as HRTEM and Grazing Incidence X-Ray Diffraction to detect possible clustering. If clustering is identified, thermal treatments may be employed to dissociate electrically inactive regions, potentially improving overall device performance. These preliminary ideas may evolve as research progresses, contributing to a deeper understanding of diffusion phenomena and optimizing the MOVPE process to enhance solar cell efficiency.



Appendix A

A.1 Integrating the Crank-Nicolson method with Newton-Raphson root-finding

In numerical methods for solving PDEs, the Crank-Nicolson method [205] is utilized as a powerful and widely employed technique, showcasing its efficacy in simulating dynamic phenomena such as heat conduction [206] and diffusion [207]. The discretization scheme lies at the core of the Crank-Nicolson method, which provides a numerical approximation of continuous PDEs. In this method, both temporal and spatial dimensions are discretized simultaneously. The discretization is typically achieved using finite difference methods, with a specific emphasis on the central difference scheme, as illustrated in Figure A.1.

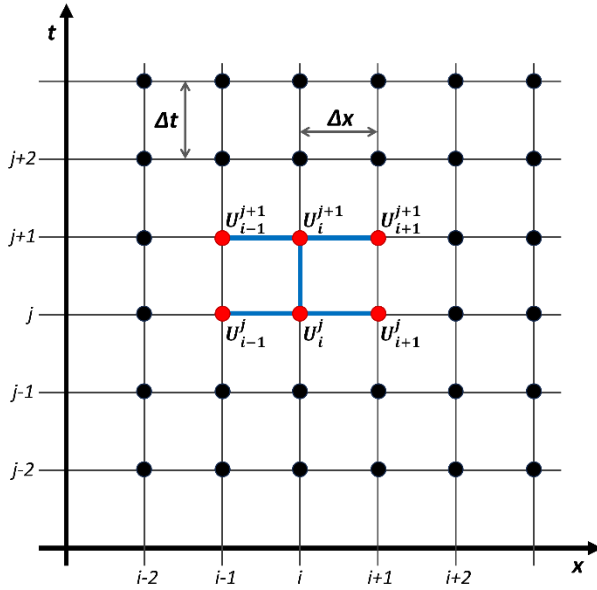


Figure A.1. Spatial (i) and time (j) discretization schematic. Δx and Δt denote spatial and time intervals. Red points connected by blue lines to calculate U_i^{j+1} .

In this figure, the suffix i represents spatial integer points separated equidistantly by the discretized interval Δx , while the suffix j means analogous points in time with an interval Δt . Each row in the figure represents the spatial array under consideration at time $j \cdot \Delta t$. Employing the central difference (red points in Figure A.1) for both time and space derivatives, the resulting equations can be expressed as:

$$\frac{\partial U}{\partial t} = \frac{U_i^{j+1} - U_i^j}{\Delta t} \quad (\text{Eq. A. 1})$$

$$\frac{\partial U}{\partial x} = \frac{U_{i+1}^j - U_{i-1}^j}{2\Delta x} \quad (\text{Eq. A. 2})$$

$$\frac{\partial U}{\partial x} = \frac{U_{i+1}^j - 2U_i^j + U_{i-1}^j}{\Delta x^2} \quad (\text{Eq. A. 3})$$

Where U_i^j is the concentration evaluated at spatial point x_i and time t_j . Setting the time derivative as a function (F) involving concentration, time, space, and the first and second derivatives of concentration:

$$\frac{\partial U}{\partial t} = F\left(U, t, x, \frac{\partial U}{\partial x}, \frac{\partial^2 U}{\partial x^2}\right) \quad (\text{Eq. A. 4})$$

The Crank-Nicholson method averages F at time steps j and $j+1$ for the same spatial point x_i . Thus, then, substituting Eq. A.1 into Eq. A.4:

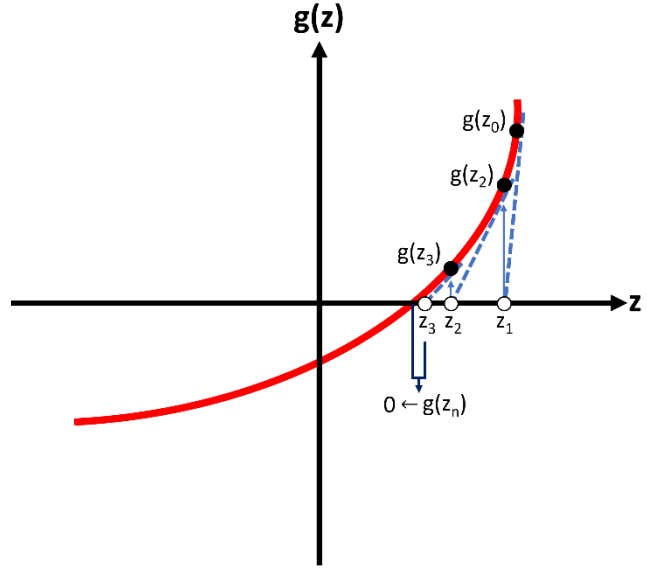
$$\frac{U_i^{j+1} - U_i^j}{\Delta t} = \frac{1}{2} \left[F_i^j \left(U, t, x, \frac{\partial U}{\partial x}, \frac{\partial^2 U}{\partial x^2} \right) + F_i^{j+1} \left(U, t, x, \frac{\partial U}{\partial x}, \frac{\partial^2 U}{\partial x^2} \right) \right] \quad (\text{Eq. A. 5})$$

Finally, combining Eq. 5.8, Eq. A.2, Eq. A.3 and Eq. A.5:

$$\begin{aligned} \frac{U_i^{j+1} - U_i^j}{\Delta t} = \frac{1}{2} & \left[\frac{\partial D(U)}{\partial U} \Big|_i^j \left(\frac{U_{i+1}^j - U_{i-1}^j}{2\Delta x} \right)^2 + D(U) \Big|_i^j \frac{U_{i+1}^j - 2U_i^j + U_{i-1}^j}{\Delta x^2} \right. \\ & + \frac{\partial D(U)}{\partial U} \Big|_i^{j+1} \left(\frac{U_{i+1}^{j+1} - U_{i-1}^{j+1}}{2\Delta x} \right)^2 \\ & \left. + D(U) \Big|_i^{j+1} \frac{U_{i+1}^{j+1} - 2U_i^{j+1} + U_{i-1}^{j+1}}{\Delta x^2} \right] \end{aligned} \quad (\text{Eq. A. 6})$$

Because solving this method using a standard matrix equation in linear algebra proves impossible, an alternative approach becomes necessary. The selected numerical root-finding method is the Newton-Raphson method. This method distinguishes itself from other methods by requiring the evaluation of both the function $g(z)$ and the derivative $\frac{dg(z)}{dz}$, at arbitrary points z . The variables g and z are used to differentiate from F and x used in previous texts. This method geometrically extends the tangent line at the current point z_p until it crosses zero, setting the next guess z_{p+1} to the abscissa of that zero crossing (see Figure A.2). Algebraically, the Newton-Raphson formula derives from the Taylor series expansion of a function in the vicinity of a point.

Figure A.2. Newton-Raphson's method extrapolates the local derivative to find the next estimate of the root.



$$g(z + \delta) = g(z) + \frac{dg(z)}{dz} \delta + \frac{1}{2} \frac{d^2g(z)}{dz^2} \delta^2 + \dots \quad (\text{Eq. A. 7})$$

For sufficiently small δ , values and well-behaved functions, the terms beyond linear become negligible, implying:

$$\delta = -\frac{g(z)}{dg(z)/dz} \quad (\text{Eq. A. 8})$$

While the previous explanations were restricted to one dimension for simplicity, the method seamlessly generalizes to multiple dimensions as Eq. A.6. A typical problem involves zeroing N functional relations, requiring variables z_p :

$$G_p(z_1, z_2, \dots, z_n) = G_p(\mathbf{z}) = 0 \quad p = 1, 2, \dots, N \quad (\text{Eq. A. 9})$$

We denote the complete vector of values z_p as $\mathbf{z}$, and the entire vector of functions G_p is represented by G . In the vicinity of $\mathbf{z}$, the function G_p can once again be expanded using a Taylor series:

$$G_p(\mathbf{z} + \delta\mathbf{z}) = G_p(\mathbf{z}) + \sum_{k=1}^N \frac{\partial G_p}{\partial z_k} \delta z_k + \mathcal{O}(\delta\mathbf{z}^2) \quad (\text{Eq. A. 10})$$

The partial derivatives appearing in Eq. A.10 belong to the Jacobian matrix J :

$$J_{p,k} \equiv \frac{\partial G_p}{\partial z_k} \quad (\text{Eq. A. 11})$$

In matrix notation, Eq. A.10 becomes:

$$\mathbf{G}(\mathbf{z} + \delta\mathbf{z}) = \mathbf{G}(\mathbf{z}) + \mathbf{J} \cdot \delta\mathbf{z} + \mathcal{O}(\delta\mathbf{z}^2) \quad (\text{Eq. A. 12})$$

By neglecting terms of order $\delta\mathbf{z}^2$ and higher and by setting $\mathbf{G}(\mathbf{z} + \delta\mathbf{z}) = 0$, a set of linear equations for the corrections $\delta\mathbf{z}$ is obtained, moving each function closer to zero simultaneously:

$$\mathbf{J} \cdot \delta\mathbf{z} = -\mathbf{G}(\mathbf{z}) \quad (\text{Eq. A. 13})$$

In matrix form, $\delta\mathbf{z}$ can be determined as $\delta\mathbf{z} = -\mathbf{J}^{-1} \cdot \mathbf{G}(\mathbf{z})$. The corrections are then added to the solution vector:

$$\mathbf{z}_{New} = \mathbf{z}_{Old} + \delta\mathbf{z} \quad (\text{Eq. A. 14})$$

This process is iterated to convergence, typically starting with an array believed to be close to the solution ($\mathbf{z}_{Old}$ in this context). Various convergence criteria exist [208], but this Thesis adopts convergence through the norm of $\delta\mathbf{z}$:

$$\|\mathbf{z}_{New} - \mathbf{z}_{Old}\| < \varepsilon \quad (\text{Eq. A. 15})$$

With ε being an arbitrary tolerance indicating when iterations should cease. In simple terms, a sufficiently low value of ε ensures highly precise solutions at each step, given that the norm of a vector is the sum of its elements raised to the square, always yielding positive values.

Now, $\mathbf{J}$ must be constructed from Eq. A.6. The array $\mathbf{z}$ for the considered case is the concentration vector at $j+1$, to be exact, $\vec{U}^{j+1}$. Considering that the spatial variables to be determined are related to $i-1$, i and $i+1$, the Jacobian matrix becomes tridiagonal, with derivatives following Eq. A.11:

$$J_{i,i} = \frac{\partial G_i}{\partial U_i^{j+1}} \quad (\text{Eq. A. 16})$$

$$J_{i,i-1} = \frac{\partial G_i}{\partial U_{i-1}^{j+1}} \quad (\text{Eq. A. 17})$$

$$J_{i,i+1} = \frac{\partial G_i}{\partial U_{i+1}^{j+1}} \quad (\text{Eq. A. 18})$$

The function G_i is simply Eq. A.6 with the temporal term in the right part of the equation, given by:

$$\begin{aligned}
 G_i = & U_i^j - U_i^{j+1} \\
 & + \frac{\Delta t}{2} \left[\frac{\partial D(U)}{\partial U} \Big|_i^j \left(\frac{U_{i+1}^j - U_{i-1}^j}{2\Delta x} \right)^2 \right. \\
 & + D(U) \Big|_i^j \frac{U_{i+1}^j - 2U_i^j + U_{i-1}^j}{\Delta x^2} \\
 & + \frac{\partial D(U)}{\partial U} \Big|_i^{j+1} \left(\frac{U_{i+1}^{j+1} - U_{i-1}^{j+1}}{2\Delta x} \right)^2 \\
 & \left. + D(U) \Big|_i^{j+1} \frac{U_{i+1}^{j+1} - 2U_i^{j+1} + U_{i-1}^{j+1}}{\Delta x^2} \right]
 \end{aligned} \tag{Eq. A. 19}$$

Substituting this into Eq. A.16, Eq. A.17 and Eq. A.18, we obtain:

$$\begin{aligned}
 J_{i,i} = & 1 - \frac{\Delta t}{2} \left[\frac{\partial}{\partial U_i^{j+1}} \left(\frac{\partial D(U)}{\partial U} \Big|_i^{j+1} \right) \left(\frac{U_{i+1}^{j+1} - U_{i-1}^{j+1}}{2\Delta x} \right)^2 \right. \\
 & \left. + \frac{\partial D(U) \Big|_i^{j+1}}{\partial U_i^{j+1}} \left(\frac{U_{i+1}^{j+1} - 2U_i^{j+1} + U_{i-1}^{j+1}}{\Delta x^2} \right) - D(U) \Big|_i^{j+1} \left(\frac{2}{\Delta x^2} \right) \right]
 \end{aligned} \tag{Eq. A. 20}$$

$$J_{i,i-1} = -\frac{\Delta t}{2} \left[-2 \frac{\partial D(U)}{\partial U} \Big|_i^{j+1} \left(\frac{U_{i+1}^{j+1} - U_{i-1}^{j+1}}{2\Delta x} \right)^2 + \frac{D(U) \Big|_i^{j+1}}{\Delta x^2} \right] \tag{Eq. A. 21}$$

$$J_{i,i+1} = -\frac{\Delta t}{2} \left[2 \frac{\partial D(U)}{\partial U} \Big|_i^{j+1} \left(\frac{U_{i+1}^{j+1} - U_{i-1}^{j+1}}{2\Delta x} \right)^2 + \frac{D(U) \Big|_i^{j+1}}{\Delta x^2} \right] \tag{Eq. A. 22}$$

In our computational framework, we utilize the tridiagonal matrix by implementing it through custom *MATLAB* code, exploiting the built-in *sparse* function for accelerated computational processing.

As for boundary conditions, the simulations detailed in this Thesis predominantly utilize Dirichlet boundary conditions. Specifically, on the left side of the integration box, the Dirichlet boundary condition dictates that the solution at adjacent points to the integration box (i.e., the semiconductor bulk in our case). For our specific scenario, this condition is represented as:

$$U(0, t) = f_0(t) \tag{Eq. A. 23}$$

In our simulation setup, we assume an infinite source of dopants (U_0), considering the substantial influx of As atoms from both the AsH₃ flow and GaAs depositions. Consequently, the function $f_0(t)$ simplifies to U_0 , leading to the conversion of Eq. A.23 as follows:

$$U_0^j = U_0 \quad (\text{Eq. A. 24})$$

It's worth noting that in the context of Eq. A.6's numbering convention, the zero term on the left implies $i = 0$ for every time step j . Furthermore, to ensure consistency across iterations, it's crucial that Eq. A.19 satisfies:

$$G_0 = U_0^{iter} - U_0 \quad (\text{Eq. A. 25})$$

Where U_0^{iter} is the value of U_0^j within the Newton-Raphson loop. By adhering to this criterion, we effectively ensure the proper implementation of the infinite source while preserving a nearly negligible δz .

To address the right side, von Neumann boundary conditions were chosen to simulate diffusing concentrations exiting the computational domain without encountering a sink or source. Importantly, the simulation operates sufficiently far from the integration box boundary, ensuring that the actual right edge is never reached during the simulation.

A.2 The fourth-order Runge-Kutta method

While the Crank-Nicolson method, coupled with the Newton-Raphson root-finding technique, has been established, an additional numerical simulation was performed to validate the final outcome. This supplementary simulation was undertaken to verify the results obtained from both methods through a comparative analysis. The Runge-Kutta method, renowned for solving differential equations, was employed for this purpose. Resuming to standard notation for variables:

$$\frac{dy}{dt} = f(y, t), \quad y(t_0) = y_0 \quad (\text{Eq. A. 26})$$

Here, y is an unknown function (scalar or vector) of time t . For the case at hand, $f(y, t)$ corresponds to the right term in Eq. 5.8.

Figure A.3 visually shows Euler's method through the representation of the blue line. This curve depicts the true form of $y(t)$, which we aim to determine. According to Eq. A.26, the slope of the solution is equal to the function $f(y, t)$. Thus, given the value of y at time t , the slope at that specific point can be estimated, as represented in the figure. Subsequently, we extend the slope to the time $t + \Delta t$, providing an estimation of the value of $y(t + \Delta t)$, indicated by * in the figure. If the curve of $y(t)$ were a straight line between t and $t + \Delta t$, this

method would yield a perfect match for $y(t + \Delta t)$. However, in the presence of curvature, the estimate becomes approximate, and the resulting error is the difference between the estimate and the true value.

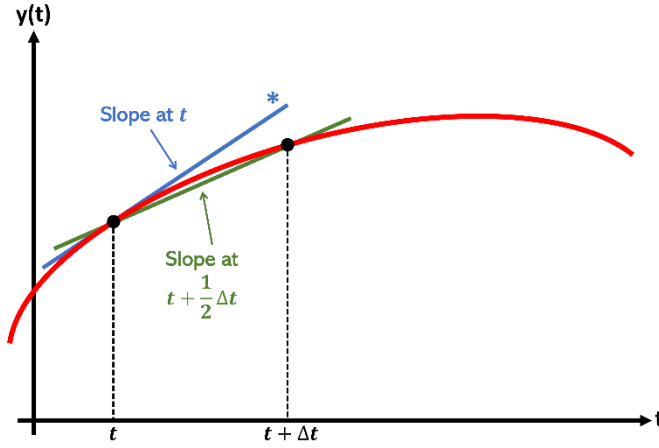


Figure A.3. Graphical representation of the (second-order) Runge-Kutta method. The blue lines depict the extension from t to $t + \Delta t$ with a slope determined by Euler's method (indicated with *). The green line represents the subsequent step of the method, where a new slope obtained at $t + \frac{1}{2}\Delta t$ provides a more accurate approximation for the red curve.

Now, let's consider a similar calculation, but utilizing the slope at the midpoint $t + \frac{1}{2}\Delta t$ for the extrapolation. Extrapolating with this slope yields a different estimate for $y(t + \Delta t)$, often significantly more accurate than Euler's method.

Once again, the method involves a Taylor expansion around $t + \frac{1}{2}\Delta t$ to determine the value of $y(t + \Delta t)$:

$$y(t + \Delta t) = y\left(t + \frac{1}{2}\Delta t\right) + \frac{1}{2}\Delta t \left(\frac{dy}{dt}\right)\Big|_{t+\frac{1}{2}\Delta t} + \frac{1}{8}\Delta t^2 \left(\frac{d^2y}{dt^2}\right)\Big|_{t+\frac{1}{2}\Delta t} + \mathcal{O}(\Delta t^3) \quad (\text{Eq. A. 27})$$

Analogously, an expression for $y(t)$ can be:

$$y(t) = y\left(t + \frac{1}{2}\Delta t\right) - \frac{1}{2}\Delta t \left(\frac{dy}{dt}\right)\Big|_{t+\frac{1}{2}\Delta t} + \frac{1}{8}\Delta t^2 \left(\frac{d^2y}{dt^2}\right)\Big|_{t+\frac{1}{2}\Delta t} + \mathcal{O}(\Delta t^3) \quad (\text{Eq. A. 28})$$

Subtracting the second expression from the first and rearranging:

$$\begin{aligned} y(t + \Delta t) &= y(t) + \Delta t \left(\frac{dy}{dt}\right)\Big|_{t+\frac{1}{2}\Delta t} + \mathcal{O}(\Delta t^3) \\ &= y(t) + \Delta t \cdot f\left(y\left(t + \frac{1}{2}\Delta t\right), t + \frac{1}{2}\Delta t\right) + \mathcal{O}(\Delta t^3) \end{aligned} \quad (\text{Eq. A. 29})$$

The error term is now $\mathcal{O}(\Delta t^3)$ due to the cancellation of the term in Δt^2 , making the approximation one factor Δt more accurate than before. When Δt is sufficiently small, this improvement can significantly enhance the accuracy of calculations.

However, a challenge arises with Eq. A.29 as it requires knowledge of $y\left(t + \frac{1}{2}\Delta t\right)$, which is unknown. To address this, we approximate $y\left(t + \frac{1}{2}\Delta t\right)$ using Euler's method $y\left(t + \frac{1}{2}\Delta t\right) = y(t) + \frac{1}{2}\Delta t \cdot f(y, t)$. Substituting this approximation into the equation, a single step in the calculation can be expressed as:

$$k_1 = \Delta t \cdot f(y, t) \quad (\text{Eq. A. 30})$$

$$k_2 = \Delta t \cdot f\left(y + \frac{1}{2}k_1, t + \frac{1}{2}\Delta t\right) \quad (\text{Eq. A. 31})$$

$$y(t + \Delta t) = y(t) + k_2 \quad (\text{Eq. A. 32})$$

These equations represent the second-order Runge-Kutta method. Expanding on this approach by performing Taylor expansions around various points and combining them appropriately, we can derive the fourth-order Runge-Kutta (RK4) method for terms above Δt^3 , expressed as:

$$k_1 = \Delta t \cdot f(y, t) \quad (\text{Eq. A. 33})$$

$$k_2 = \Delta t \cdot f\left(y + \frac{1}{2}k_1, t + \frac{1}{2}\Delta t\right) \quad (\text{Eq. A. 34})$$

$$k_3 = \Delta t \cdot f\left(y + \frac{1}{2}k_2, t + \frac{1}{2}\Delta t\right) \quad (\text{Eq. A. 35})$$

$$k_4 = \Delta t \cdot f(y + k_3, t + \Delta t) \quad (\text{Eq. A. 36})$$

$$y(t + \Delta t) = y(t) + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad (\text{Eq. A. 37})$$

Naturally, this presents a comprehensive overview of the RK4 method, taking into account the discretization and terminology established in the preceding section. The system of equations (Eq. A.33-Eq. A.37) can be reformulated as follows:

$$k_1 = \Delta t \cdot f(U_i^j, t^j) \quad (\text{Eq. A. 38})$$

$$k_2 = \Delta t \cdot f\left(U_i^j + \frac{1}{2}k_1, t^j + \frac{1}{2}\Delta t\right) \quad (\text{Eq. A. 39})$$

$$k_3 = \Delta t \cdot f\left(U_i^j + \frac{1}{2}k_2, t^j + \frac{1}{2}\Delta t\right) \quad (\text{Eq. A. 40})$$

$$k_4 = \Delta t \cdot f(U_i^j + k_3, t^j + \Delta t) \quad (\text{Eq. A. 41})$$

$$U_i^{j+1} = U_i^j + \frac{1}{6}(k_1 + 2k_2 + 2k_3 + k_4) \quad (\text{Eq. A. 42})$$

With $t^j = j \cdot \Delta t$ expressing the entire time array in the simulation.

Continuing with the boundary conditions, Dirichlet conditions were applied on the left side and Neumann conditions on the right side, following the same approach as in the previous method.

A.3 Comparison between numerical methods

Once the final algebraic equations have been obtained, it becomes important to check the stability of the Crank-Nicolson method. In numerical methods, stability ensures that errors introduced at one time step do not escalate during subsequent computations. Thankfully, the Crank-Nicolson method itself is commonly recognized for its unconditional stability [208]. However, the combination of this approach with the Newton-Raphson root-finding technique may introduce instability owing to the inherent characteristics of the root-finding method. This is because instability in the Newton-Raphson method can cause rapid divergence, making accurate root finding difficult or even impossible. Similarly, instability in the RK4 method can result in increasingly inaccurate results as integration progresses. In summary, while both methods can suffer from instability, its impact may be more severe with Newton-Raphson, affecting the convergence of the root-finding process directly. Conversely, instability in the RK4 method primarily affects the accuracy of the computed solution over time. However, spatial and temporal intervals were carefully selected to meet stability criteria, as outlined in the Crank-Nicolson method (where $1/2 \leq D\Delta t/\Delta x^2$), which is employed in both numerical methods. This ensures dependable numerical computations in both instances.

Throughout the code development and validation process, a specific challenge arose concerning the application of the Newton-Raphson method. This issue manifested as

instabilities in the obtained solutions, potentially attributed to the stiffness of our non-linear PDE [209]. The concept of stiffness in differential equations is often context-dependent, with solutions tailored to the unique characteristics of each scenario. Stiffness generally arises when there are widely differing time scales within a system of differential equations, meaning that different Δt may be required for time steps. Essentially, it occurs when certain components of the system evolve significantly faster than others, potentially resulting in numerical instability or inefficiency during numerical solution methods. One potential approach is to address the stiffness by transforming the PDE into a dimensionless form. To achieve this, the variables U , x and t are scaled as follows: $U = \mu U_0$, $x = \chi L$ and $t = \tau t_f$. Here, μ , χ and τ represent the dimensionless variables, while L and t_f denote the final length where simulation occurs and the time at which the simulated diffusion finishes, respectively. U_0 stands for the initial concentration. Additionally, the spatial and time intervals are normalized, yielding $\Delta\chi = \Delta x/L$ and $\Delta\tau = \Delta t/t_f$. Upon applying these transformations to Eq. 5.8:

$$\frac{\partial\mu}{\partial\tau} = \frac{t_f}{L^2} \left[\frac{\partial D(\mu)}{\partial\mu} \left(\frac{\partial\mu}{\partial\chi} \right)^2 + D(\mu) \frac{\partial^2\mu}{\partial\chi^2} \right] \quad (Eq. A.43)$$

This transformation maintains the validity of the previous explanation, and the preceding text remains valid for this purpose.

Given that the methods employed here rely on truncation error, thorough comparisons of outputs are highly recommended. The accuracy of these methods is contingent on the truncation error in both spatial and temporal intervals. In spatial steps, both methods adopt the central finite difference method, inherently associated with a truncation error of $\mathcal{O}(\Delta x^2)$. The noteworthy discrepancy arises in the truncation error of the time interval. The Crank-Nicolson method, akin to finite difference, truncates the Taylor series just after the linear term, resulting in an associated error of $\mathcal{O}(\Delta t^2)$. Conversely, as explained through the slope approach, RK4 extends the Taylor series beyond the quadratic term to $\mathcal{O}(\Delta t^5)$. Considering each error in tandem with its corresponding method, we find that for Crank-Nicolson plus Newton-Raphson method, the error is $\mathcal{O}(\Delta x^2) + \mathcal{O}(\Delta t^2)$, and for RK4, is $\mathcal{O}(\Delta x^2) + \mathcal{O}(\Delta t^5)$. Consequently, RK4 yields more accurate results as Δt decreases.

To ensure the validity and comparability of the results obtained from these two methods, comparative numerical simulations were run under two scenarios: constant diffusivity and linearly concentration-dependent diffusivity, i.e., the independent term in Eq. 5.5 with and without the right term with $m=1$ in the sum. As Eq. 5.1 indicates, diffusivity also depends on temperature. Hence, a constant temperature of 700 °C over 10 min is arbitrarily chosen. The boundary conditions involve an infinite source U_0 of 10^{19} cm^{-3} adjacent to the left side of the

integration box. Initial conditions comprise a null quantity of the diffusing element in the integration box. Finally, the values of activation energy and the pre-exponential factor for the two selected examples are tabulated in table A.I. In the case of the linearly concentration-dependent diffusivity, n_i was maintained at 10^{18} cm^{-3} and, every incoming diffusing element was considered active, namely, $U = n$. Simulations are shown in Figure A.4.

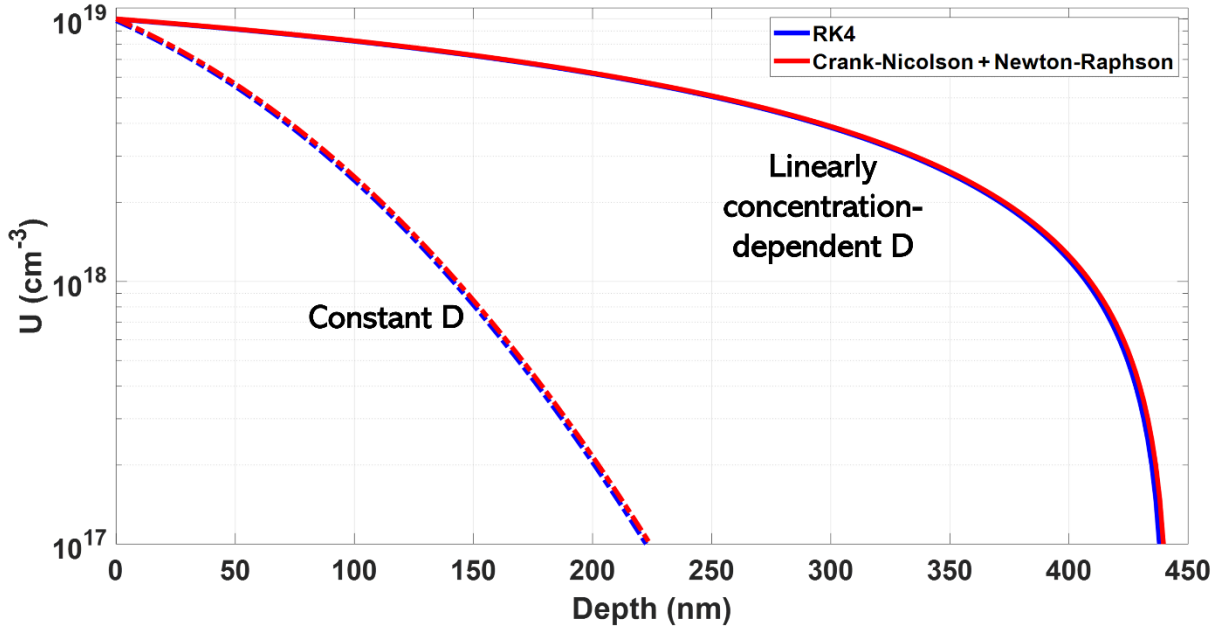
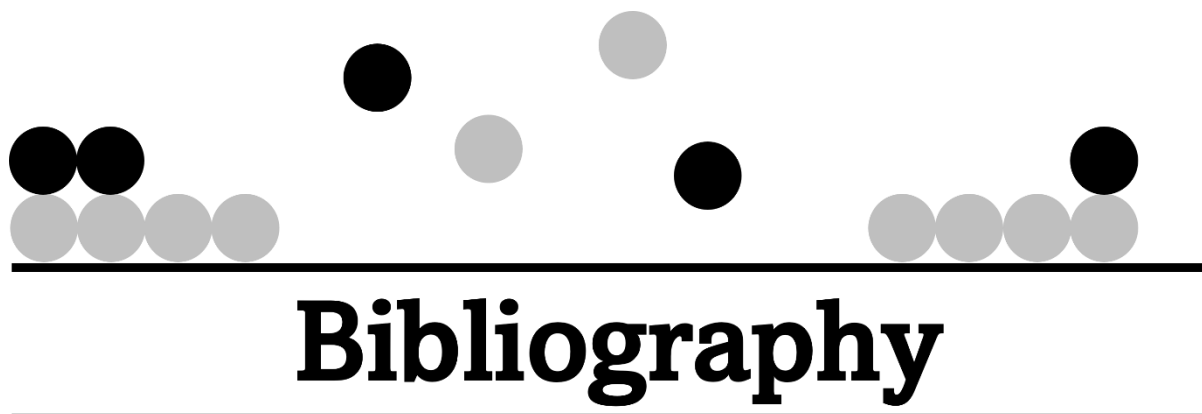


Figure A.4. Resultant simulations following the parameters indicated in Table V.I for constant diffusivity (dash-dotted line) and linearly concentration-dependent diffusivity (solid line). For these simulations, the value of L is $0.5 \mu\text{m}$.

Observably, both methods yield virtually identical results, with RK4 showing slightly slower profile. This small discrepancy may be attributed to the different nature of each method in providing solutions. For instance, the higher accumulative error for the Crank-Nicolson and Newton-Raphson methods, whose time truncation error, as recently mentioned, is three orders of magnitude higher (Δt^5 vs Δt^2). This discrepancy can be resolved by diminishing the value of Δx or Δt , but it would entail a higher time-consuming simulation to minimize this insignificant difference. Especially noteworthy is that RK4 is 8.5 times faster in computational considerations for these specific simulations. Hence, both methods are considered closely aligned, indicating a higher probability of accurately describing and simulating diffusion phenomena.

	Constant diffusivity	Linearly concentration-dependent diffusivity
D_0^0 ($\mu m^2 s^{-1}$)	1	1
E_a^0 (eV)	1	1.5
D_0^{1-} ($\mu m^2 s^{-1}$)	-	2
E_a^{1-} (eV)	-	1

Table A.I. Arbitrary values of activation energy and the pre-exponential factor for the two selected examples, with resultant simulations presented in Figure A.4. Superscripts 0 and 1- indicate parameters for the vacancy state of charges in a neutral or single negative state, respectively. The explanation of this can be read in Section 5.1.



-
- [1] Climate change 2021: the physical science basis : summary for policymakers : working group I contribution to the sixth Assessment report of the Intergovernmental Panel on Climate Change. Geneva, Switzerland: IPCC, 2021.
 - [2] H. H. Aumann, A. Ruzmaikin, and J. Teixeira, "Frequency of severe storms and global warming," *Geophysical Research Letters*, vol. 35, no. 19, p. 2008GL034562, Oct. 2008, doi: 10.1029/2008GL034562.
 - [3] A. Dai, "Drought under global warming: a review," *WIREs Climate Change*, vol. 2, no. 1, pp. 45–65, Jan. 2011, doi: 10.1002/wcc.81.
 - [4] J. R. Malcolm, C. Liu, R. P. Neilson, L. Hansen, and L. Hannah, "Global Warming and Extinctions of Endemic Species from Biodiversity Hotspots," *Conservation Biology*, vol. 20, no. 2, pp. 538–548, Apr. 2006, doi: 10.1111/j.1523-1739.2006.00364.x.
 - [5] J. Jewell, V. Vinichenko, L. Nacke, and A. Cherp, "Prospects for powering past coal," *Nat. Clim. Chang.*, vol. 9, no. 8, pp. 592–597, Aug. 2019, doi: 10.1038/s41558-019-0509-6.
 - [6] M. K. Jangra, K. P. S. Parmar, and N. K. Yadav, "Reduction of Global Warming By Using Renewable Energy Resources: A Mathematic Approach," vol. 3, no. 2.
 - [7] J. L. Simon, *The ultimate resource 2*. Princeton University Press, 1996.
 - [8] R. W. Bentley, "Global oil & gas depletion: an overview," *Energy Policy*, vol. 30, no. 3, pp. 189–205, Feb. 2002, doi: 10.1016/S0301-4215(01)00144-6.
 - [9] C. Smith, "The finiteness of crude oil: Are we running out?," *SURG*, vol. 11, Aug. 2019, doi: 10.21083/surg.v11i0.5225.
 - [10] J. Hassler, P. Krusell, and C. Olovsson, "Finite resources and the world economy," *Journal of International Economics*, vol. 136, p. 103592, May 2022, doi: 10.1016/j.jinteco.2022.103592.
 - [11] X. A. Rodríguez and C. Arias, "The effects of resource depletion on coal mining productivity," *Energy Economics*, vol. 30, no. 2, pp. 397–408, Mar. 2008, doi: 10.1016/j.eneco.2007.10.007.
 - [12] F. R. Martins, R. Rüther, E. B. Pereira, and S. L. Abreu, "Solar energy scenarios in Brazil. Part two: Photovoltaics applications," *Energy Policy*, vol. 36, no. 8, pp. 2865–2877, Aug. 2008, doi: 10.1016/j.enpol.2008.04.001.

-
- [13] P. D. Rigo, J. C. M. Siluk, D. P. Lacerda, G. Rediske, and C. B. Rosa, "A model for measuring the success of distributed small-scale photovoltaic systems projects," *Solar Energy*, vol. 205, pp. 241–253, Jul. 2020, doi: 10.1016/j.solener.2020.04.078.
- [14] A. Zahedi, "Maximizing solar PV energy penetration using energy storage technology," *Renewable and Sustainable Energy Reviews*, vol. 15, no. 1, pp. 866–870, Jan. 2011, doi: 10.1016/j.rser.2010.09.011.
- [15] S. Adachi, *Properties of semiconductor alloys: group-IV, III-V and II-VI semiconductors*, 1. ed. in *Wiley series in materials for electronic & optoelectronic applications*. Chichester: Wiley, 2009.
- [16] M. Tanenbaum, "Diffused Emitter and Base Silicon," *THE BELL SYSTEM TECHNICAL JOURNAL*, 1956.
- [17] J. T. Clemens, "Silicon microelectronics technology," *Bell Labs Tech. J.*, vol. 2, no. 4, pp. 76–102, Aug. 2002, doi: 10.1002/bltj.2084.
- [18] Y. Yu et al., "Review of silicon recovery in the photovoltaic industry," *Current Opinion in Green and Sustainable Chemistry*, vol. 44, p. 100870, Dec. 2023, doi: 10.1016/j.cogsc.2023.100870.
- [19] A. A. Yaroshevsky, "Abundances of chemical elements in the Earth's crust," *Geochem. Int.*, vol. 44, no. 1, pp. 48–55, Jan. 2006, doi: 10.1134/S001670290601006X.
- [20] S. Oda and D. Ferry, *Silicon Nanoelectronics*. CRC Press, 2017.
- [21] A. Müller, M. Ghosh, R. Sonnenschein, and P. Woditsch, "Silicon for photovoltaic applications," *Materials Science and Engineering: B*, vol. 134, no. 2–3, pp. 257–262, Oct. 2006, doi: 10.1016/j.mseb.2006.06.054.
- [22] M. A. Green, "Silicon photovoltaic modules: a brief history of the first 50 years," *Prog. Photovolt: Res. Appl.*, vol. 13, no. 5, pp. 447–455, Aug. 2005, doi: 10.1002/pip.612.
- [23] W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells," *Journal of Applied Physics*, vol. 32, no. 3, pp. 510–519, Mar. 1961, doi: 10.1063/1.1736034.
- [24] T. Tiedje, E. Yablonovitch, G. D. Cody, and B. G. Brooks, "Limiting efficiency of silicon solar cells," *IEEE Trans. Electron Devices*, vol. 31, no. 5, pp. 711–716, May 1984, doi: 10.1109/T-ED.1984.21594.
- [25] M. A. Green et al., "Solar cell efficiency tables (version 62)," *Progress in Photovoltaics: Research and Applications*, vol. 31, no. 7, pp. 651–663, 2023, doi: 10.1002/pip.3726.

-
- [26] V. Sorianello et al., "Germanium on insulator near-infrared photodetectors fabricated by layer transfer," *Thin Solid Films*, vol. 518, no. 9, Art. no. 9, Feb. 2010, doi: 10.1016/j.tsf.2009.09.134.
- [27] P. Chiu, I. Shih, S. Shi, and P. Laou, "Study of laser reflection of infrared cameras with germanium optics," presented at the Targets and Backgrounds IX: Characterization and Representation, SPIE, 2003, pp. 190–199.
- [28] P. Gansauge, "Double diffused high-speed germanium transistors," *IEEE Trans. Electron Devices*, vol. 15, no. 10, Art. no. 10, Oct. 1968, doi: 10.1109/T-ED.1968.16505.
- [29] S. Lischke, "Ultra-fast germanium photodiode with 3-dB bandwidth of 265 GHz," *Nature Photonics*, vol. 15, 2021.
- [30] N. E. Posthuma, G. Flamand, and J. Poortmans, "Development of stand-alone germanium solar cells for application in space using spin-on diffusants".
- [31] T. Burger, C. Sempere, B. Roy-Layinde, and A. Lenert, "Present Efficiencies and Future Opportunities in Thermophotovoltaics," *Joule*, vol. 4, no. 8, Art. no. 8, Aug. 2020, doi: 10.1016/j.joule.2020.06.021.
- [32] T. Nagashima, K. Okumura, K. Murata, and M. Yamaguchi, "A germanium back-contact type cell for thermophotovoltaic applications".
- [33] V. M. Andreev, "GaAs and High-Efficiency Space Cells".
- [34] J. Li et al., "A Brief Review of High Efficiency III-V Solar Cells for Space Application," *Front. Phys.*, vol. 8, p. 631925, Feb. 2021, doi: 10.3389/fphy.2020.631925.
- [35] A. W. Bett, F. Dimroth, G. Stollwerck, and O. V. Sulima, "III-V compounds for solar cell applications," *Applied Physics A: Materials Science & Processing*, vol. 69, no. 2, Art. no. 2, Aug. 1999, doi: 10.1007/s003390050983.
- [36] C. Chu, P. Iles, and W. Patterson, "Recent advances in GaAs/Ge solar cells," presented at the NASA. Lewis Research Center, Space Photovoltaic Research and Technology Conference, 1991.
- [37] R. R. King et al., "40% efficient metamorphic GaInP/GaInAs/Ge multijunction solar cells," *Applied Physics Letters*, vol. 90, no. 18, p. 183516, Apr. 2007, doi: 10.1063/1.2734507.
- [38] R. Höll, M. Kling, and E. Schroll, "Metallogenesis of germanium—A review," *Ore Geology Reviews*, vol. 30, no. 3, pp. 145–180, Mar. 2007, doi: 10.1016/j.oregeorev.2005.07.034.

-
- [39] S. Mauthe et al., "High-speed III-V nanowire photodetector monolithically integrated on Si," *Nat Commun*, vol. 11, no. 1, Art. no. 1, Sep. 2020, doi: 10.1038/s41467-020-18374-z.
 - [40] K. Tanabe, K. Watanabe, and Y. Arakawa, "III-V/Si hybrid photonic devices by direct fusion bonding," *Sci Rep*, vol. 2, no. 1, Art. no. 1, Apr. 2012, doi: 10.1038/srep00349.
 - [41] L. M. Giovane, H.-C. Luan, A. M. Agarwal, and L. C. Kimerling, "Correlation between leakage current density and threading dislocation density in SiGe p-i-n diodes grown on relaxed graded buffer layers," *Applied Physics Letters*, vol. 78, no. 4, pp. 541–543, Jan. 2001, doi: 10.1063/1.1341230.
 - [42] S. Fan, D. Jung, Y. Sun, B. D. Li, D. Martin-Martin, and M. L. Lee, "16.8%-Efficient n^+/p GaAs Solar Cells on Si With High Short-Circuit Current Density," *IEEE J. Photovoltaics*, vol. 9, no. 3, pp. 660–665, May 2019, doi: 10.1109/JPHOTOV.2019.2894657.
 - [43] J.E. Ayers, T. Kujofsa, P. Rago, and J. Raphael, *Heteroepitaxy of semiconductors: theory, growth, and characterization*. CRC press, 2016.
 - [44] D. Jung, P. G. Callahan, B. Shin, K. Mukherjee, A. C. Gossard, and J. E. Bowers, "Low threading dislocation density GaAs growth on on-axis GaP/Si (001)," *Journal of Applied Physics*, vol. 122, no. 22, p. 225703, Dec. 2017, doi: 10.1063/1.5001360.
 - [45] Y. Kim et al., "GaAs/Si Tandem Solar Cells with an Optically Transparent InAlAs/GaAs Strained Layer Superlattices Dislocation Filter Layer," *Energies*, vol. 16, no. 3, Art. no. 3, Jan. 2023, doi: 10.3390/en16031158.
 - [46] S. Fan et al., "Towards High-Efficiency GaAsP/Si Tandem Cells," in *2017 IEEE 44th Photovoltaic Specialist Conference (PVSC)*, Jun. 2017, pp. 3376–3380. doi: 10.1109/PVSC.2017.8366555.
 - [47] M. Feifel et al., "Epitaxial GaInP/GaAs/Si Triple-Junction Solar Cell with 25.9% AM1.5g Efficiency Enabled by Transparent Metamorphic $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$ Step-Graded Buffer Structures," *Solar RRL*, vol. 5, no. 5, p. 2000763, 2021, doi: 10.1002/solr.202000763.
 - [48] "Comparison of Direct Growth and Wafer Bonding for the Fabrication of GaInP/GaAs Dual-Junction Solar Cells on Silicon | IEEE Journals & Magazine | IEEE Xplore." Accessed: Apr. 30, 2024. [Online]. Available: <https://ieeexplore.ieee.org/abstract/document/6736084>
 - [49] T. J. Grassman, D. J. Chmielewski, J. A. Carlin, and S. A. Ringel, "Development of epitaxial 2- and 3-junction III-V/Si solar cells," in *2016 IEEE 43rd Photovoltaic Specialists*

- Conference (PVSC), Portland, OR, USA: IEEE, Jun. 2016, pp. 2036–2039. doi: 10.1109/PVSC.2016.7749986.
- [50] M. Feifel, D. Lackner, J. Ohlmann, J. Benick, M. Hermle, and F. Dimroth, “Direct Growth of a GaInP/GaAs/Si Triple-Junction Solar Cell with 22.3% AM1.5g Efficiency,” *Solar RRL*, vol. 3, no. 12, Art. no. 12, 2019, doi: <https://doi.org/10.1002/solr.201900313>.
- [51] T. J. Grassman et al., “Toward >25% Efficient Monolithic Epitaxial GaAsP/Si Tandem Solar Cells,” in 2019 IEEE 46th Photovoltaic Specialists Conference (PVSC), Chicago, IL, USA: IEEE, Jun. 2019, pp. 0734–0737. doi: 10.1109/PVSC40753.2019.8980574.
- [52] S. Fan et al., “20%-efficient epitaxial GaAsP/Si tandem solar cells,” *Solar Energy Materials and Solar Cells*, vol. 202, p. 110144, Nov. 2019, doi: 10.1016/j.solmat.2019.110144.
- [53] M. Yamaguchi, “Potential and present status of III–V/Si tandem solar cells,” in 2014 IEEE 40th Photovoltaic Specialist Conference (PVSC), Jun. 2014, pp. 0821–0826. doi: 10.1109/PVSC.2014.6925041.
- [54] D. B. Holt, “DEVICE EFFECTS OF DISLOCATIONS,” *J. Phys. Colloques*, vol. 40, no. C6, pp. C6-199, Jun. 1979, doi: 10.1051/jphyscol:1979639.
- [55] I. Kudman and R. Paff, “Thermal expansion of $\text{In}_x\text{Ga}_{1-x}\text{P}$ alloys,” *Journal of Applied Physics*, vol. 43, no. 9, pp. 3760–3762, 1972.
- [56] J. L. Liu, S. Tong, Y. H. Luo, J. Wan, and K. L. Wang, “High-quality Ge films on Si substrates using Sb surfactant-mediated graded SiGe buffers,” *Applied Physics Letters*, vol. 79, no. 21, pp. 3431–3433, Nov. 2001, doi: 10.1063/1.1421092.
- [57] M. T. Currie, S. B. Samavedam, T. A. Langdo, C. W. Leitz, and E. A. Fitzgerald, “Controlling threading dislocation densities in Ge on Si using graded SiGe layers and chemical-mechanical polishing,” *Applied Physics Letters*, vol. 72, no. 14, pp. 1718–1720, Apr. 1998, doi: 10.1063/1.121162.
- [58] I. Rey-Stolle, E. Barrigón, B. Galiana, and C. Algora, “Analysis of germanium epitaxial wafers for III–V heteroepitaxy,” *Journal of Crystal Growth*, vol. 310, no. 23, pp. 4803–4807, Nov. 2008, doi: 10.1016/j.jcrysgro.2008.07.116.
- [59] Q. L. Liu, C. W. Zhao, Y. M. Xing, S. J. Su, and B. W. Cheng, “Quantitative strain analysis of misfit dislocations in a Ge/Si heterostructure interface by geometric phase analysis,” *Optics and Lasers in Engineering*, vol. 50, no. 5, pp. 796–799, May 2012, doi: 10.1016/j.optlaseng.2011.12.009.

- [60] Y. Fukuda and Y. Kohama, "High quality heteroepitaxial Ge growth on (100) Si by MBE," *Journal of Crystal Growth*, vol. 81, no. 1, pp. 451–457, Feb. 1987, doi: 10.1016/0022-0248(87)90432-5.
- [61] P. Liu et al., "High-quality Ge film grown on Si substrate and its thermodynamic mechanism," *Vacuum*, vol. 186, p. 110068, Apr. 2021, doi: 10.1016/j.vacuum.2021.110068.
- [62] K. H. Lee, A. Jandl, Y. H. Tan, E. A. Fitzgerald, and C. S. Tan, "Growth and characterization of germanium epitaxial film on silicon (001) with germane precursor in metal organic chemical vapour deposition (MOCVD) chamber," *AIP Advances*, vol. 3, no. 9, p. 092123, Sep. 2013, doi: 10.1063/1.4822424.
- [63] Y. Yamamoto, P. Zaumseil, M. A. Schubert, and B. Tillack, "Influence of annealing conditions on threading dislocation density in Ge deposited on Si by reduced pressure chemical vapor deposition," *Semicond. Sci. Technol.*, vol. 33, no. 12, p. 124007, Oct. 2018, doi: 10.1088/1361-6641/aae574.
- [64] Y. Yamamoto, P. Zaumseil, T. Arguirov, M. Kittler, and B. Tillack, "Low threading dislocation density Ge deposited on Si (1 0 0) using RPCVD," *Solid-State Electronics*, vol. 60, no. 1, pp. 2–6, Jun. 2011, doi: 10.1016/j.sse.2011.01.032.
- [65] O. Skibitzki et al., "Reduction of threading dislocation density beyond the saturation limit by optimized reverse grading," *Phys. Rev. Mater.*, vol. 4, no. 10, p. 103403, Oct. 2020, doi: 10.1103/PhysRevMaterials.4.103403.
- [66] K. H. Lee et al., "Reduction of threading dislocation density in Ge/Si using a heavily As-doped Ge seed layer," *AIP Advances*, vol. 6, no. 2, p. 025028, Feb. 2016, doi: 10.1063/1.4943218.
- [67] M. F. B. Amin, T. Hizawa, J. A. Piedra-Lorenzana, T. Nakai, and Y. Ishikawa, "Reduced Threading Dislocation Density in a Ge Epitaxial Film on a Submicron-Patterned Si Substrate Grown by Chemical Vapor Deposition," *J. Electron. Mater.*, vol. 52, no. 8, pp. 5059–5065, Aug. 2023, doi: 10.1007/s11664-023-10302-3.
- [68] Y. Wang et al., "Fabrication and characterization of single junction GaAs solar cells on Si with As-doped Ge buffer," *Solar Energy Materials and Solar Cells*, vol. 172, pp. 140–144, 2017.
- [69] R. Ginige et al., "Characterization of Ge-on-Si virtual substrates and single junction GaAs solar cells," *Semicond. Sci. Technol.*, vol. 21, no. 6, pp. 775–780, Jun. 2006, doi: 10.1088/0268-1242/21/6/011.

-
- [70] T. W. Kim, B. R. Albert, L. C. Kimerling, and J. Michel, "InGaP solar cell on Ge-on-Si virtual substrate for novel solar power conversion," *Journal of Applied Physics*, vol. 123, no. 8, p. 085111, Feb. 2018, doi: 10.1063/1.5018082.
- [71] M. J. Archer et al., "Ga In P / Ga As dual junction solar cells on Ge/Si epitaxial templates," *Applied Physics Letters*, vol. 92, no. 10, p. 103503, Mar. 2008, doi: 10.1063/1.2887904.
- [72] A. Scaccabarozzi et al., "Integration of InGaP/GaAs/Ge triple-junction solar cells on deeply patterned silicon substrates," *Progress in Photovoltaics: Research and Applications*, vol. 24, no. 10, pp. 1368–1377, 2016.
- [73] E. V. Johnson, G. Patriarche, and P. Roca i Cabarrocas, "Directional growth of Ge on GaAs at 175°C using plasma-generated nanocrystals," *Applied Physics Letters*, vol. 92, no. 10, p. 103108, Mar. 2008, doi: 10.1063/1.2895636.
- [74] T. Ward et al., "Design rules for dislocation filters," *Journal of Applied Physics*, vol. 116, no. 6, p. 063508, Aug. 2014, doi: 10.1063/1.4892162.
- [75] R. Cariou, R. Ruggeri, X. Tan, G. Mannino, and J. Nassar, "Structural properties of relaxed thin film germanium layers grown by low temperature RF-PECVD epitaxy on Si and Ge (100) substrates," *AIP Advances*, p. 8, 2014.
- [76] M. Yamaguchi and C. Amano, "Efficiency calculations of thin-film GaAs solar cells on Si substrates," *Journal of Applied Physics*, vol. 58, no. 9, pp. 3601–3606, Nov. 1985, doi: 10.1063/1.335737.
- [77] E. F. Schubert, *Light-Emitting Diodes*, 2nd ed. Cambridge: Cambridge University Press, 2006. doi: 10.1017/CBO9780511790546.
- [78] M. Sotoodeh, A. H. Khalid, and A. A. Rezazadeh, "Empirical low-field mobility model for III–V compounds applicable in device simulation codes," *Journal of Applied Physics*, vol. 87, no. 6, pp. 2890–2900, Mar. 2000, doi: 10.1063/1.372274.
- [79] Y. P. Varshni, "Band-to-Band Radiative Recombination in Groups IV, VI, and III-V Semiconductors (I)," *physica status solidi (b)*, vol. 19, no. 2, pp. 459–514, 1967, doi: 10.1002/pssb.19670190202.
- [80] R. Dagan, Y. Rosenwaks, A. Kribus, A. W. Walker, J. Ohlmann, and F. Dimroth, "Minority carrier recombination of ordered Ga_{0.51}In_{0.49}P at high temperatures," *Applied Physics Letters*, vol. 109, no. 22, p. 222106, Dec. 2016, doi: 10.1063/1.4971282.

- [81] W. J. Yang, Z. Q. Ma, X. Tang, C. B. Feng, W. G. Zhao, and P. P. Shi, "Internal quantum efficiency for solar cells," *Solar Energy*, vol. 82, no. 2, pp. 106–110, Feb. 2008, doi: 10.1016/j.solener.2007.07.010.
- [82] A. Fach, J. John, P. Müller, C. Paglino, and H. Zogg, "Material properties of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ epilayers on Si and their correlation with the performance of infrared photodiodes," *J. Electron. Mater.*, vol. 26, no. 7, pp. 873–877, Jul. 1997, doi: 10.1007/s11664-997-0266-6.
- [83] L. Barrutia, I. García, E. Barrigón, M. Ochoa, I. Lombardero, M. Hinojosa, P. Caño, J. Bautista, L. Cifuentes, I. Rey-Stolle, C. Algora, "Development of the Lattice Matched GaInP/GaInAs/Ge Triple Junction Solar Cell with an Efficiency Over 40%," in 2018 Spanish Conference on Electron Devices (CDE), Salamanca: IEEE, Nov. 2018, pp. 1–4. doi: 10.1109/CDE.2018.8596996.
- [84] I. García, I. Rey-Stolle, B. Galiana, and C. Algora, "A 32.6% efficient lattice-matched dual-junction solar cell working at 1000 suns," *Applied Physics Letters*, vol. 94, no. 5, p. 053509, Feb. 2009, doi: 10.1063/1.3078817.
- [85] M. Hinojosa, I. Lombardero, C. Algora, and I. García, "Improved GaInP/GaAs/GaInAs inverted metamorphic triple-junction solar cells by reduction of Zn diffusion in the top subcell," *Solar Energy Materials and Solar Cells*, vol. 248, p. 112000, Dec. 2022, doi: 10.1016/j.solmat.2022.112000.
- [86] G. J. Hou, E. García-Tabarés, I. García, and I. Rey-Stolle, "High-low refractive index stacks as antireflection coatings on triple-junction solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 31, no. 1, pp. 62–70, 2023, doi: 10.1002/pip.3608.
- [87] L. Barrutia, I. García, E. Barrigón, M. Ochoa, C. Algora, and I. Rey-Stolle, "Impact of the III-V/Ge nucleation routine on the performance of high efficiency multijunction solar cells," *Solar Energy Materials and Solar Cells*, vol. 207, p. 110355, Apr. 2020, doi: 10.1016/j.solmat.2019.110355.
- [88] E. Barrigon, B. Galiana, and I. Rey-Stolle, "Reflectance anisotropy spectroscopy assessment of the MOVPE nucleation of GaInP on germanium (1 0 0)," *Journal of Crystal Growth*, vol. 315, no. 1, Art. no. 1, Jan. 2011, doi: 10.1016/j.jcrysgro.2010.09.038.

-
- [89] B. Galiana, I. Rey-Stolle, C. Algora, K. Volz, and W. Stolz, "A GaAs metalorganic vapor phase epitaxy growth process to reduce Ge outdiffusion from the Ge substrate," *Appl. Phys. Lett.*, vol. 92, no. 15, Art. no. 15, Apr. 2008, doi: 10.1063/1.2901029.
 - [90] K. Horowitz, M. Woodhouse, H. Lee, and G. Smestad, "Bottom-Up Cost Analysis of a High Concentration PV Module: NREL (National Renewable Energy Laboratory)," 2015, Accessed: Mar. 28, 2024. [Online]. Available: <https://research-hub.nrel.gov/en/publications/bottom-up-cost-analysis-of-a-high-concentration-pv-module-nrel-na>
 - [91] B. Smith, "Development and Life Cycle Assessment of Advanced-Concept III-V Multijunction Photovoltaics," Theses, Jun. 2018, [Online]. Available: <https://repository.rit.edu/theses/9877>
 - [92] I. Garcia et al., "Ge virtual substrates for high efficiency III-V solar cells: applications, potential and challenges," in 2019 IEEE 46th Photovoltaic Specialists Conference (PVSC), Chicago, IL, USA: IEEE, Jun. 2019, pp. 1444–1451. doi: 10.1109/PVSC40753.2019.8980914.
 - [93] I. Garcia et al., "Space III-V Multijunction Solar Cells on Ge/Si virtual substrates," in 2019 European Space Power Conference (ESPC), Juan-les-Pins, France: IEEE, Sep. 2019, pp. 1–6. Accessed: Feb. 01, 2021. [Online]. Available: <https://ieeexplore.ieee.org/document/8932026/>
 - [94] I. García, L. Barrutia, S. Dadgostar, M. Hinojosa, A. Johnson, and I. Rey-Stolle, "Thinned GaInP/GaInAs/Ge solar cells grown with reduced cracking on Ge|Si virtual substrates," *Solar Energy Materials and Solar Cells*, p. 10, 2021.
 - [95] E. Barrigón, P. Espinet-González, Y. Contreras, and I. Rey-Stolle, "Implications of low breakdown voltage of component subcells on external quantum efficiency measurements of multijunction solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 23, no. 11, pp. 1597–1607, 2015, doi: 10.1002/pip.2597.
 - [96] I. García, M. Ghosh, V. Orejuela, R. i C. Pere, and I. Rey-Stolle, "III-V multijunction solar cells on ultrathin Ge|Si virtual substrates grown at low temperature by RF-PECVD," presented at the European PV Solar Energy Conference and Exhibition (EUPVSEC), p. 4.
 - [97] M. Ghosh et al., "Ultrathin Ge epilayers on Si produced by low-temperature PECVD acting as virtual substrates for III-V / c-Si tandem solar cells," *Solar Energy Materials and Solar Cells*, vol. 236, p. 111535, Mar. 2022, doi: 10.1016/j.solmat.2021.111535.

- [98] N. Milenkovic et al., "20% efficient solar cells fabricated from epitaxially grown and freestanding n-type wafers," *Solar Energy Materials and Solar Cells*, vol. 159, pp. 570–575, Jan. 2017, doi: 10.1016/j.solmat.2016.09.044.
- [99] British Geological Survey, Bureau de Recherches Géologiques et Minières, Deloitte Sustainability, Directorate-General for Internal Market, Industry, Entrepreneurship and SMEs (European Commission), and TNO, Study on the review of the list of critical raw materials: final report. Publications Office of the European Union, 2017. Accessed: Mar. 29, 2024. [Online]. Available: <https://data.europa.eu/doi/10.2873/876644>
- [100] G. Courtois et al., "Development of germanium-on-germanium engineered substrates for III-V multijunction solar cells," in 2020 47th IEEE Photovoltaic Specialists Conference (PVSC), Jun. 2020, pp. 1053–1055. doi: 10.1109/PVSC45281.2020.9300462.
- [101] R. Kurstjens et al., "GaInP solar cells grown on Ge-on-Ge engineered substrates," in 2021 IEEE 48th Photovoltaic Specialists Conference (PVSC), Jun. 2021, pp. 0175–0177. doi: 10.1109/PVSC43889.2021.9518407.
- [102] H. M. Manasevit, "SINGLE-CRYSTAL GALLIUM ARSENIDE ON INSULATING SUBSTRATES," *Applied Physics Letters*, vol. 12, no. 4, pp. 156–159, Feb. 1968, doi: 10.1063/1.1651934.
- [103] G. B. Stringfellow, "Organometallic Vapor-Phase Epitaxy: Theory and Practice," Aug. 1989. Accessed: Apr. 19, 2024. [Online]. Available: <https://www.semanticscholar.org/paper/Organometallic-Vapor-Phase-Epitaxy%3A-Theory-and-Stringfellow/74f671ab1f2f2d348b7ffedf69913bfaf4c9930d>
- [104] P. Roca i Cabarrocas, J. B. Chévrier, J. Huc, A. Lloret, J. Y. Parey, and J. P. M. Schmitt, "A fully automated hot-wall multiplasma-monochamber reactor for thin film deposition," *Journal of Vacuum Science & Technology A*, vol. 9, no. 4, pp. 2331–2341, Jul. 1991, doi: 10.1116/1.577318.
- [105] P. Weightman, D. S. Martin, R. J. Cole, and T. Farrell, "Reflection anisotropy spectroscopy," *Rep. Prog. Phys.*, vol. 68, no. 6, pp. 1251–1341, Jun. 2005, doi: 10.1088/0034-4885/68/6/R01.
- [106] W. Richter, "In-situ observation of MOVPE epitaxial growth," *Appl Phys A*, vol. 75, no. 1, pp. 129–140, Jul. 2002, doi: 10.1007/s003390101061.
- [107] D. E. Aspnes, E. Colas, A. A. Studna, R. Bhat, M. A. Koza, and V. G. Keramidas, "Kinetic Limits of Monolayer Growth on (001) Gaas by Organometallic Chemical-vapor

- Deposition," *Phys. Rev. Lett.*, vol. 61, no. 24, pp. 2782–2785, Dec. 1988, doi: 10.1103/PhysRevLett.61.2782.
- [108] L. Töben, T. Hannappel, K. Möller, H.-J. Crawack, C. Pettenkofer, and F. Willig, "RDS, LEED and STM of the P-rich and Ga-rich surfaces of GaP(1 0 0)," *Surface Science*, vol. 494, no. 1, pp. L755–L760, Nov. 2001, doi: 10.1016/S0039-6028(01)01492-3.
- [109] P. Kurpas, M. Sato, A. Knauer, and M. Weyers, "On-line growth monitoring of InP-based device structures by reflectance anisotropy spectroscopy," *Journal of Electronic Materials*, vol. 26, no. 10, p. 1154, 1997.
- [110] L. Daweritz and K. Ploog, "Contribution of reflection high-energy electron diffraction to nanometre tailoring of surfaces and interfaces by molecular beam epitaxy," *Semicond. Sci. Technol.*, vol. 9, no. 2, p. 123, Feb. 1994, doi: 10.1088/0268-1242/9/2/001.
- [111] P. P. Notten, "Electrochemical study of the etching of III-V semiconductors," 1989, doi: 10.6100/IR307988.
- [112] V. Mihailetschi et al., "High efficiency industrial screen printed N-type mc-Si solar cells with front boron emitter," *Conference Record of the IEEE Photovoltaic Specialists Conference*, pp. 1–5, May 2008, doi: 10.1109/PVSC.2008.4922846.
- [113] G. W. Eldridge et al., "Carrier diffusion effects in III–V semiconductor structures measured by the point contact current voltage technique," *Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena*, vol. 10, no. 1, pp. 463–467, Jan. 1992, doi: 10.1116/1.586375.
- [114] V. Gopal, E.-H. Chen, E. P. Kvam, and J. M. Woodall, "Electrochemical capacitance voltage profiling of the narrow band gap semiconductor InAs," *J. Electron. Mater.*, vol. 29, no. 11, pp. 1333–1339, Nov. 2000, doi: 10.1007/s11664-000-0134-0.
- [115] S. Sioncke et al., "Etch Rates of Ge, GaAs and InGaAs in Acids, Bases and Peroxide Based Mixtures," *ECS Trans.*, vol. 16, no. 10, p. 451, Oct. 2008, doi: 10.1149/1.2986802.
- [116] A. Engel, H. E. Gaub, and D. J. Müller, "Atomic force microscopy: A forceful way with single molecules," *Current Biology*, vol. 9, no. 4, pp. R133–R136, Feb. 1999, doi: 10.1016/S0960-9822(99)80081-5.
- [117] B. Galiana et al., "Compositional analysis and evolution of defects formed on GaInP epilayers grown on Germanium," *Superlattices and Microstructures*, vol. 45, no. 4, pp. 277–284, Apr. 2009, doi: 10.1016/j.spmi.2008.12.013.

- [118] H. Sodabanlu, G. Li, K. Watanabe, Y. Nakano, and M. Sugiyama, "Improvement of InGaP solar cells grown with TBP in planetary MOVPE reactor," *Solar Energy Materials and Solar Cells*, vol. 257, p. 112402, Aug. 2023, doi: 10.1016/j.solmat.2023.112402.
- [119] "Convergent-Beam Electron Diffraction for Local Lattice Parameters in III-V Semiconductors." Accessed: Apr. 23, 2024. [Online]. Available: https://www.jstage.jst.go.jp/article/matertrans1989/31/7/31_7_641/_article/-char/ja/
- [120] F. Louchet, J. Pelissier, D. Caillard, J. P. Peyrade, C. Levade, and G. Vanderschaeve, "In situ TEM study of dislocation mobility in semiconducting materials," *Microsc. Microanal. Microstruct.*, vol. 4, no. 2–3, pp. 199–210, Apr. 1993, doi: 10.1051/mmm:0199300402-3019900.
- [121] W. Li et al., "Effect of rapid thermal annealing on threading dislocation density in III-V epilayers monolithically grown on silicon," *Journal of Applied Physics*, vol. 123, no. 21, p. 215303, Jun. 2018, doi: 10.1063/1.5011161.
- [122] Z. Liliental-Weber and R. P. Mariella, "Characterization of GaAs/Si/GaAs Heterointerfaces," *MRS Online Proceedings Library (OPL)*, vol. 148, p. 241, Jan. 1989, doi: 10.1557/PROC-148-241.
- [123] P. Caroff, M. E. Messing, B. M. Borg, K. A. Dick, K. Deppert, and L.-E. Wernersson, "InSb heterostructure nanowires: MOVPE growth under extreme lattice mismatch," *Nanotechnology*, vol. 20, no. 49, p. 495606, Nov. 2009, doi: 10.1088/0957-4484/20/49/495606.
- [124] D. Cherns, W. T. Young, and F. A. Ponce, "Characterisation of dislocations, nanopipes and inversion domains in GaN by transmission electron microscopy," *Materials Science and Engineering: B*, vol. 50, no. 1, pp. 76–81, Dec. 1997, doi: 10.1016/S0921-5107(97)00171-2.
- [125] X. J. Su et al., "Identifying dislocations and stacking faults in GaN films by scanning transmission electron microscopy," *Mater. Res. Express*, vol. 3, no. 8, p. 086401, Aug. 2016, doi: 10.1088/2053-1591/3/8/086401.
- [126] B. Saha and P. Chakraborty, "MCsnp+-SIMS: An Innovative Approach for Direct Compositional Analysis of Materials without Standards," *Energy Procedia*, vol. 41, pp. 80–109, Dec. 2013, doi: 10.1016/j.egypro.2013.09.009.

- [127] H. H. Silvestri, H. Bracht, J. L. Hansen, A. N. Larsen, and E. E. Haller, "Diffusion of silicon in crystalline germanium," *Semicond. Sci. Technol.*, vol. 21, no. 6, p. 758, Apr. 2006, doi: 10.1088/0268-1242/21/6/008.
- [128] J. C. Lee et al., "Investigations of semiconductor devices using SIMS; diffusion, contamination, process control," *Applied Surface Science*, vol. 255, no. 4, pp. 1395–1399, Dec. 2008, doi: 10.1016/j.apsusc.2008.06.129.
- [129] V. Vasil'ev, G. Gagas, K. Soboleva, and V. Kuchinskii, "Formation of A3B5 ternary solid solutions on GaSb plates by solid- state substitution reactions," *Journal of Physics: Conference Series*, vol. 572, Dec. 2014, doi: 10.1088/1742-6596/572/1/012033.
- [130] R. Kamaladasa, "Basic Principles and Application of Electron Channeling in a Scanning Electron Microscope for Dislocation Analysis," 2010. Accessed: Apr. 23, 2024. [Online]. Available: <https://www.semanticscholar.org/paper/Basic-Principles-and-Application-of-Electron-in-a-Kamaladasa/b678fd2bf57de97f6c7775b779971d7bc8478584>
- [131] K. N. Yaung et al., "Threading dislocation density characterization in III–V photovoltaic materials by electron channeling contrast imaging," *Journal of Crystal Growth*, vol. 453, pp. 65–70, Nov. 2016, doi: 10.1016/j.jcrysgro.2016.08.015.
- [132] J. Yang et al., "Thin Ge buffer layer on silicon for integration of III-V on silicon," *Journal of Crystal Growth*, vol. 514, pp. 109–113, May 2019, doi: 10.1016/j.jcrysgro.2019.02.044.
- [133] *Electron Backscatter Diffraction in Materials Science*. Accessed: Apr. 25, 2024. [Online]. Available: <https://link.springer.com/book/10.1007/978-0-387-88136-2>
- [134] K. P. Mingard et al., "Comparison of EBSD and conventional methods of grain size measurement of hardmetals," *International Journal of Refractory Metals and Hard Materials*, vol. 27, no. 2, pp. 213–223, Mar. 2009, doi: 10.1016/j.ijrmhm.2008.06.009.
- [135] Y. Shao et al., "EBSD crystallographic orientation research on strain distribution in hydride vapor phase epitaxy GaN grown on patterned substrate," *CrystEngComm*, vol. 15, no. 39, pp. 7965–7969, Sep. 2013, doi: 10.1039/C3CE40802G.
- [136] P. Martín, V. Orejuela, C. Sanchez-Perez, I. García, and I. Rey-Stolle, "Device Architectures for Germanium TPV Cells with Efficiencies over 30%," in *2023 14th Spanish Conference on Electron Devices (CDE)*, Valencia, Spain: IEEE, Jun. 2023, pp. 1–4. doi: 10.1109/CDE58627.2023.10339503.
- [137] P. Caño et al., "GaAsP/SiGe tandem solar cells on porous Si substrates," *Solar Energy*, vol. 230, pp. 925–934, Dec. 2021, doi: 10.1016/j.solener.2021.10.075.

- [138] B. Galiana, I. Rey-Stolle, M. Baudrit, I. García, and C. Algora, "A comparative study of BSF layers for GaAs-based single-junction or multijunction concentrator solar cells," *Semicond. Sci. Technol.*, vol. 21, no. 10, p. 1387, Aug. 2006, doi: 10.1088/0268-1242/21/10/003.
- [139] C. Algora et al., "Advances in Flexible and Lightweight 3J Space Solar Cells for High Power Density Applications," in 2023 13th European Space Power Conference (ESPC), Oct. 2023, pp. 1–4. doi: 10.1109/ESPC59009.2023.10298177.
- [140] Y. S. Li and J. Nguyen, "Tensilely Strained Ge Films on Si Substrates Created by Physical Vapor Deposition of Solid Sources," *Sci Rep*, vol. 8, no. 1, p. 16734, Nov. 2018, doi: 10.1038/s41598-018-35224-7.
- [141] T. Karabacak, "Thin-film growth dynamics with shadowing and re-emission effects," *JNP*, vol. 5, no. 1, p. 052501, Jan. 2011, doi: 10.1117/1.3543822.
- [142] W.-K. Burton, N. t Cabrera, and F. Frank, "The growth of crystals and the equilibrium structure of their surfaces," *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, vol. 243, no. 866, pp. 299–358, 1951.
- [143] Y. B. Bolkhovityanov, A. S. Deryabin, A. K. Gutakovskii, and L. V. Sokolov, "Mechanism of induced nucleation of misfit dislocations in the Ge-on-Si(0 0 1) system and its role in the formation of the core structure of edge misfit dislocations," *Acta Materialia*, vol. 61, no. 2, pp. 617–621, Jan. 2013, doi: 10.1016/j.actamat.2012.09.082.
- [144] S. Oktyabrsky, H. Wu, R. D. Vispute, and J. Narayan, "Misfit dislocations in low-temperature grown Ge/Si heterostructures," *Philosophical Magazine A*, vol. 71, no. 3, pp. 537–551, Mar. 1995, doi: 10.1080/01418619508244467.
- [145] M. Tamura, "Two groups of misfit dislocations in GaAs on Si," *Appl. Phys. A*, vol. 63, no. 4, pp. 359–370, Oct. 1996, doi: 10.1007/BF01567327.
- [146] S. F. Fang et al., "Gallium arsenide and other compound semiconductors on silicon," *Journal of Applied Physics*, vol. 68, no. 7, pp. R31–R58, Oct. 1990, doi: 10.1063/1.346284.
- [147] Z. De-Gang et al., "Effect of Interface Roughness and Dislocation Density on Electroluminescence Intensity of InGaN Multiple Quantum Wells," *Chinese Phys. Lett.*, vol. 25, no. 11, pp. 4143–4146, Nov. 2008, doi: 10.1088/0256-307X/25/11/083.
- [148] L. Scholtz, L. Ladanyi, and J. Mullerova, "Influence of Surface Roughness on Optical Characteristics of Multilayer Solar Cells," *AEEE*, vol. 12, no. 6, pp. 631–638, Jan. 2015, doi: 10.15598/aeee.v12i6.1078.

- [149] J. Krč, M. Zeman, O. Kluth, F. Smole, and M. Topič, "Effect of surface roughness of ZnO:Al films on light scattering in hydrogenated amorphous silicon solar cells," *Thin Solid Films*, vol. 426, no. 1, pp. 296–304, Feb. 2003, doi: 10.1016/S0040-6090(03)00006-3.
- [150] Y. Buzynin et al., "GaAs/Ge/Si epitaxial substrates: Development and characteristics," *AIP Advances*, vol. 7, no. 1, p. 015304, Jan. 2017, doi: 10.1063/1.4974498.
- [151] M. B. Whitwick, T. Tiedje, and T. Li, "Linear smoothing of GaAs(1 0 0) during epitaxial growth on rough substrates," *Journal of Crystal Growth*, vol. 310, no. 13, pp. 3192–3196, Jun. 2008, doi: 10.1016/j.jcrysgro.2008.03.019.
- [152] A. G. Cullis, "Strain-Induced Modulations in the Surface Morphology of Heteroepitaxial Layers," *MRS Bull.*, vol. 21, no. 4, pp. 21–26, Apr. 1996, doi: 10.1557/S0883769400035296.
- [153] J.-F. He et al., "Molecular beam epitaxy growth of GaAs on an offcut Ge substrate," *Chinese Phys. B*, vol. 20, no. 1, p. 018102, Jan. 2011, doi: 10.1088/1674-1056/20/1/018102.
- [154] F. J. Schultes et al., "Temperature dependence of diffusion length, lifetime and minority electron mobility in GaInP," *Applied Physics Letters*, vol. 103, no. 24, p. 242106, Dec. 2013, doi: 10.1063/1.4847635.
- [155] M. Niemeyer et al., "Minority carrier diffusion length, lifetime and mobility in p-type GaAs and GaInAs," *Journal of Applied Physics*, vol. 122, no. 11, p. 115702, Sep. 2017, doi: 10.1063/1.5002630.
- [156] V. Depauw, C. Porret, M. Moelants, E. Vecchio, K. Kennes, H. Han, R. Loo, J. Cho, G. Courtois, R. Kurstjens, K. Dessein, V. Orejuela, C. Sanchez-Perez, I. Rey-Stolle, I. García, "Wafer-scale Ge epitaxial foils grown at high growth rates and released from porous substrates for triple-junction solar cells," *Progress in Photovoltaics: Research and Applications*, vol. 31, no. 12, pp. 1315–1328, 2023, doi: 10.1002/pip.3634.
- [157] A. Seeger and K. P. Chik, "DIFFUSION MECHANISMS AND POINT DEFECTS IN SILICON AND GERMANIUM.," *Phys. Status Solidi*, 29: 455-542(Oct. 1, 1968)., Jan. 1968, doi: 10.1002/pssb.19680290202.
- [158] N. A. Stolwijk and L. Lerner, "Vacancy properties in germanium probed by cobalt diffusion," *Journal of Applied Physics*, vol. 110, no. 3, p. 033526, Aug. 2011, doi: 10.1063/1.3609070.

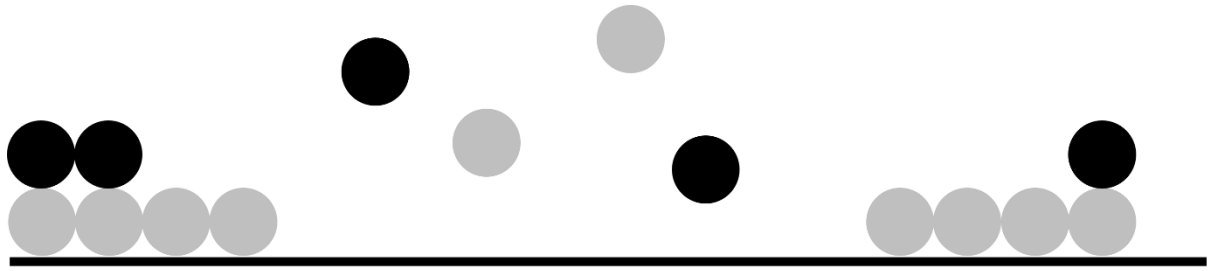
- [159] D. Shaw, "Self- and impurity diffusion in Ge and Si," *physica status solidi (b)*, vol. 72, no. 1, pp. 11–39, 1975, doi: 10.1002/pssb.2220720102.
- [160] C. L. Claeys and E. Simoen, Eds., *Germanium-based technologies: from materials to devices*. Amsterdam ; Boston: Elsevier, 2007.
- [161] H. Bracht and S. Brotzmann, "Atomic transport in germanium and the mechanism of arsenic diffusion," *Materials Science in Semiconductor Processing*, vol. 9, no. 4–5, Art. no. 4–5, Aug. 2006, doi: 10.1016/j.mssp.2006.08.041.
- [162] J. Vanhellemont and E. Simoen, "On the diffusion and activation of n-type dopants in Ge," *Materials Science in Semiconductor Processing*, vol. 15, no. 6, Art. no. 6, Dec. 2012, doi: 10.1016/j.mssp.2012.06.014.
- [163] I. Riihimäki, A. Virtanen, S. Rinta-Anttila, P. Pusa, J. Räisänen, and T. ISOLDE Collaboration, "Vacancy-impurity complexes and diffusion of Ga and Sn in intrinsic and p-doped germanium," *Applied Physics Letters*, vol. 91, no. 9, p. 091922, Aug. 2007, doi: 10.1063/1.2778540.
- [164] A. Chroneos and H. Bracht, "Diffusion of n -type dopants in germanium," *Applied Physics Reviews*, vol. 1, no. 1, Art. no. 1, Mar. 2014, doi: 10.1063/1.4838215.
- [165] P. Dorner, W. Gust, A. Lodding, H. Odelius, B. Predel, and U. Roll, "SIMS study of volume diffusion for Al in Ge.)," *ACTA METALLURG.*, vol. 30, no. 5, pp. 941–946, 1982.
- [166] K. Ahlborn, "DIFFUSION OF GALLIUM IN GERMANIUM ALONG DISLOCATIONS," *J. Phys. Colloques*, vol. 40, no. C6, pp. C6-185-C6-188, Jun. 1979, doi: 10.1051/jphyscol:1979638.
- [167] R. Kube, H. Bracht, A. Chroneos, M. Posselt, and B. Schmidt, "Intrinsic and extrinsic diffusion of indium in germanium," *Journal of Applied Physics*, vol. 106, no. 6, p. 063534, Sep. 2009, doi: 10.1063/1.3226860.
- [168] A. Chroneos, H. Bracht, R. W. Grimes, and B. P. Uberuaga, "Vacancy-mediated dopant diffusion activation enthalpies for germanium," *Applied Physics Letters*, vol. 92, no. 17, p. 172103, Apr. 2008, doi: 10.1063/1.2918842.
- [169] H. Tahini, A. Chroneos, R. W. Grimes, U. Schwingenschlögl, and H. Bracht, "Diffusion of E centers in germanium predicted using GGA+U approach," *Applied Physics Letters*, vol. 99, no. 7, p. 072112, Aug. 2011, doi: 10.1063/1.3625939.
- [170] M. Posselt et al., "P implantation into preamorphized germanium and subsequent annealing: Solid phase epitaxial regrowth, P diffusion, and activation," *Journal of*

- Vacuum Science & Technology B: Microelectronics and Nanometer Structures Processing, Measurement, and Phenomena, vol. 26, no. 1, pp. 430–434, Feb. 2008, doi: 10.1116/1.2805249.
- [171] S. Koffel et al., “Experiments and simulation of the diffusion and activation of the n-type dopants P, As, and Sb implanted into germanium,” *Microelectronic Engineering*, vol. 88, no. 4, Art. no. 4, Apr. 2011, doi: 10.1016/j.mee.2010.09.023.
- [172] A. Chroneos, R. W. Grimes, B. P. Uberuaga, S. Brotzmann, and H. Bracht, “Vacancy-arsenic clusters in germanium,” *Applied Physics Letters*, vol. 91, no. 19, Art. no. 19, Nov. 2007, doi: 10.1063/1.2805773.
- [173] D. J. Friedman and J. M. Olson, “Analysis of Ge junctions for GaInP/GaAs/Ge three-junction solar cells,” *Prog. Photovolt: Res. Appl.*, vol. 9, no. 3, Art. no. 3, May 2001, doi: 10.1002/pip.365.
- [174] D. J. Roulston, N. D. Arora, and S. G. Chamberlain, “Modeling and measurement of minority-carrier lifetime versus doping in diffused layers of n+-p silicon diodes,” *IEEE Transactions on Electron Devices*, vol. 29, no. 2, pp. 284–291, Feb. 1982, doi: 10.1109/T-ED.1982.20697.
- [175] R. H. Rediker, S. Stopek, and J. H. R. Ward, “Interface-alloy epitaxial heterojunctions,” *Solid-State Electronics*, vol. 7, no. 8, pp. 621–622, Aug. 1964, doi: 10.1016/0038-1101(64)90106-6.
- [176] H. Bracht, “Self- and foreign-atom diffusion in semiconductor isotope heterostructures. I. Continuum theoretical calculations,” *Phys. Rev. B*, vol. 75, no. 3, p. 035210, Jan. 2007, doi: 10.1103/PhysRevB.75.035210.
- [177] S. Hu, “*Phys. Status Solidi B*,” 1973.
- [178] S. Lany and A. Zunger, “Accurate prediction of defect properties in density functional supercell calculations,” *Modelling Simul. Mater. Sci. Eng.*, vol. 17, no. 8, p. 084002, Nov. 2009, doi: 10.1088/0965-0393/17/8/084002.
- [179] T. Canneaux, D. Mathiot, J.-P. Ponpon, and Y. Leroy, “Modeling of phosphorus diffusion in Ge accounting for a cubic dependence of the diffusivity with the electron concentration,” *Thin Solid Films*, vol. 518, no. 9, pp. 2394–2397, Feb. 2010, doi: 10.1016/j.tsf.2009.09.171.
- [180] M. Takenaka, K. Morii, M. Sugiyama, Y. Nakano, and S. Takagi, “Gas Phase Doping of Arsenic into (100), (110), and (111) Germanium Substrates Using a Metal–Organic

- Source,” *Jpn. J. Appl. Phys.*, vol. 50, no. 1R, Art. no. 1R, Jan. 2011, doi: 10.1143/JJAP.50.010105.
- [181] T. Liu and M. K. Orlowski, “Arsenic diffusion in boron-doped germanium,” *Electronics Letters*, vol. 49, no. 2, pp. 154–156, 2013, doi: 10.1049/el.2012.3444.
- [182] S. Brotzmann and H. Bracht, “Intrinsic and extrinsic diffusion of phosphorus, arsenic, and antimony in germanium,” *Journal of Applied Physics*, vol. 103, no. 3, Art. no. 3, Feb. 2008, doi: 10.1063/1.2837103.
- [183] K. Sarma, R. Dalby, K. Rose, O. Aina, W. Katz, and N. Lewis, “Ge diffusion at Ge/GaAs heterojunctions,” *Journal of Applied Physics*, vol. 56, no. 10, pp. 2703–2707, Nov. 1984, doi: 10.1063/1.333792.
- [184] R. S. Bauer and J. C. Mikkelsen, “Surface processes controlling MBE heterojunction formation: GaAs(100)/Ge interfaces,” *Journal of Vacuum Science and Technology*, vol. 21, no. 2, pp. 491–497, Jul. 1982, doi: 10.1116/1.571745.
- [185] I. T. Yoon, S. Y. Han, H. L. Park, and T. W. Kim, “Amphoteric behavior of Ge dopants in In_{0.5}Ga_{0.5}P epilayers grown on GaAs(100) substrates,” *Journal of Physics and Chemistry of Solids*, vol. 62, no. 3, pp. 607–611, Mar. 2001, doi: 10.1016/S0022-3697(00)00224-9.
- [186] N. Chand, J. Klem, T. Henderson, and H. Morkoç, “Diffusion of As and Ge during growth of GaAs on Ge substrate by molecular-beam epitaxy: Its effect on the device electrical characteristics,” *Journal of Applied Physics*, vol. 59, no. 10, Art. no. 10, May 1986, doi: 10.1063/1.336790.
- [187] R. M. Sieg, S. A. Ringel, S. M. Ting, E. A. Fitzgerald, and R. N. Sacks, “Anti-phase domain-free growth of GaAs on offcut (001) Ge wafers by molecular beam epitaxy with suppressed Ge outdiffusion,” *Journal of Elec Materi*, vol. 27, no. 7, pp. 900–907, Jul. 1998, doi: 10.1007/s11664-998-0116-1.
- [188] C. Frigeri, G. Atrolini, C. Pelosi, and F. Longo, “Relationship Between Crystal Defects, Ge Outdiffusion and V/III Ratio in MOVPE Grown (001) GaAs/Ge,” *MRS Online Proceedings Library (OPL)*, vol. 319, p. 135, Jan. 1993, doi: 10.1557/PROC-319-135.
- [189] P. Martín, C. Sanchez-Perez, I. García, and I. Rey-Stolle, “Maximizing infrared reflectance in germanium TPV cells,” presented at the 18TH INTERNATIONAL CONFERENCE ON CONCENTRATOR PHOTOVOLTAIC SYSTEMS (CPV-18) AND 13TH WORLD CONFERENCE ON THERMOPHOTOVOLTAIC GENERATION OF ELECTRICITY (TPV-13), Miyazaki, Japan, 2023, p. 070002. doi: 10.1063/5.0146898.

- [190] E. Barrigon, B. Galiana, and I. Rey-Stolle, "Reflectance anisotropy spectroscopy assessment of the MOVPE nucleation of GaInP on germanium (1 0 0)," *Journal of Crystal Growth*, vol. 315, no. 1, pp. 22–27, Jan. 2011, doi: 10.1016/j.jcrysgro.2010.09.038.
- [191] S. Gan, L. Li, M. J. Begarney, D. Law, B.-K. Han, and R. F. Hicks, "Step structure of arsenic-terminated vicinal Ge (100)," *Journal of Applied Physics*, vol. 85, no. 3, pp. 2004–2006, Feb. 1999, doi: 10.1063/1.369176.
- [192] T. T. Chiang and W. E. Spicer, "Arsenic on GaAs: Fermi-level pinning and thermal desorption studies," *Journal of Vacuum Science & Technology A*, vol. 7, no. 3, Art. no. 3, May 1989, doi: 10.1116/1.575874.
- [193] H. Kroemer, "Polar-on-nonpolar epitaxy," *Journal of Crystal Growth*, vol. 81, no. 1, Art. no. 1, Feb. 1987, doi: 10.1016/0022-0248(87)90391-5.
- [194] E. Barrigón, S. Brückner, O. Supplie, H. Döscher, I. Rey-Stolle, and T. Hannappel, "In situ study of Ge(100) surfaces with tertiarybutylphosphine supply in vapor phase epitaxy ambient," *Journal of Crystal Growth*, vol. 370, pp. 173–176, May 2013, doi: 10.1016/j.jcrysgro.2012.07.046.
- [195] A. Paszuk et al., "Atomic surface control of Ge(100) in MOCVD reactors coated with (Ga)As residuals," *Applied Surface Science*, vol. 565, p. 150513, Nov. 2021, doi: 10.1016/j.apsusc.2021.150513.
- [196] W. E. McMahon and J. M. Olson, "Atomic-resolution STM study of a structural phase transition of steps on vicinal As/Ge(100)," *Phys. Rev. B*, vol. 60, no. 23, Art. no. 23, Dec. 1999, doi: 10.1103/PhysRevB.60.15999.
- [197] J. Oh and J. C. Campbell, "Thermal desorption of Ge native oxides and the loss of Ge from the surface," *Journal of Elec Materi*, vol. 33, no. 4, Art. no. 4, Apr. 2004, doi: 10.1007/s11664-004-0144-4.
- [198] P. Tsouroutas, D. Tsoukalas, I. Zergioti, N. Cherkashin, and A. Claverie, "Diffusion and activation of phosphorus in germanium," *Materials Science in Semiconductor Processing*, vol. 11, no. 5, pp. 372–377, Oct. 2008, doi: 10.1016/j.mssp.2008.09.005.
- [199] P. Tsouroutas, D. Tsoukalas, I. Zergioti, N. Cherkashin, and A. Claverie, "Modeling and experiments on diffusion and activation of phosphorus in germanium," *Journal of Applied Physics*, vol. 105, no. 9, p. 094910, May 2009, doi: 10.1063/1.3117485.

-
- [200] E. Simoen and J. Vanhellemont, "On the diffusion and activation of ion-implanted n-type dopants in germanium," *Journal of Applied Physics*, vol. 106, no. 10, p. 103516, Nov. 2009, doi: 10.1063/1.3261838.
- [201] S. Mitha, M. J. Aziz, D. Schiferl, and D. B. Poker, "Activation volume for arsenic diffusion in germanium," *Appl. Phys. Lett.*, vol. 69, no. 7, Art. no. 7, Aug. 1996, doi: 10.1063/1.116944.
- [202] Y. P. Varshni, "Temperature dependence of the energy gap in semiconductors," *Physica*, vol. 34, no. 1, pp. 149–154, Jan. 1967, doi: 10.1016/0031-8914(67)90062-6.
- [203] W. E. McMahon and J. M. Olson, "Atomic-resolution STM study of a structural phase transition of steps on vicinal As/Ge(100)," *Phys. Rev. B*, vol. 60, no. 23, pp. 15999–16005, Dec. 1999, doi: 10.1103/PhysRevB.60.15999.
- [204] E. García-Tabarés, D. Martín, I. García, and I. Rey-Stolle, "Understanding phosphorus diffusion into silicon in a MOVPE environment for III–V on silicon solar cells," *Solar Energy Materials and Solar Cells*, vol. 116, pp. 61–67, Sep. 2013, doi: 10.1016/j.solmat.2013.04.003.
- [205] J. Crank and P. Nicolson, "A practical method for numerical evaluation of solutions of partial differential equations of the heat-conduction type," *Mathematical Proceedings of the Cambridge Philosophical Society*, vol. 43, no. 1, pp. 50–67, Jan. 1947, doi: 10.1017/S0305004100023197.
- [206] T. Cebeci, *Convective Heat Transfer*. Horizons Pub., 2002.
- [207] M. Dehghan, "Crank–Nicolson finite difference method for two-dimensional diffusion with an integral condition," *Applied Mathematics and Computation*, vol. 124, no. 1, pp. 17–27, Nov. 2001, doi: 10.1016/S0096-3003(00)00031-X.
- [208] W. H. Press, Ed., *Numerical recipes: the art of scientific computing*, 3. ed. Cambridge: Cambridge University Press, 2007.
- [209] L. F. Shampine and C. W. Gear, "A User's View of Solving Stiff Ordinary Differential Equations," *SIAM Review*, vol. 21, no. 1, p. 17, 1979, doi: 10.1137/1021001.



Publications and conferences

Publications

This section will list both the scientific articles and proceedings, authored as principal author or co-author, along with my contributions to conferences. In the digital version of this thesis, access to these documents and the corresponding conference programs will be provided. To access the materials, click on the DOI number for articles and proceedings, and click on the title for conference programs.

- **V. Orejuela**, E. García-Tabares, I. Rey-Stolle, and I. García, “Arsenic Diffusion in MOVPE-Grown GaAs/Ge Epitaxial Structures,” *Advanced Electronic Materials*, vol. n/a, no. n/a, p. 2400021, doi: [10.1002/aelm.202400021](https://doi.org/10.1002/aelm.202400021).
- **V. Orejuela**, I. García, C. Sanchez-Perez, M. Hinojosa, S. Dadgostar, M. Ghosh, P. Roca i Cabarrocas and, I. Rey-Stolle, “Advances in the development of high efficiency III-V multijunction solar cells on Ge|Si virtual substrates,” in *2021 13th Spanish Conference on Electron Devices (CDE)*, Jun. 2021, pp. 27–32. doi: [10.1109/CDE52135.2021.9455736](https://doi.org/10.1109/CDE52135.2021.9455736).
- P. Martín, **V. Orejuela**, C. Sanchez-Perez, I. García, and I. Rey-Stolle, “Device Architectures for Germanium TPV Cells with Efficiencies over 30%,” in *2023 14th Spanish Conference on Electron Devices (CDE)*, Jun. 2023, pp. 1–4. doi: [10.1109/CDE58627.2023.10339503](https://doi.org/10.1109/CDE58627.2023.10339503).
- P. Martin, **V. Orejuela**, A. Cano, I. García, A. Luque, and I. Rey-Stolle, “Cost-Effective 23.2% Efficient Germanium Thermophotovoltaic Converters for Thermal Batteries.” Rochester, NY, May 22, 2024. doi: [10.2139/ssrn.4836762](https://doi.org/10.2139/ssrn.4836762). (At the time of writing this thesis, this document was under peer review, and a pre-print version is available)
- I. García, A. Cano, P. Martín, **V. Orejuela**, and I. Rey-Stolle, “n/p and p/n InGaAs cells for high density TPV modules,” *Solar Energy Materials and Solar Cells*, vol. 271, p. 112863, Jul. 2024, doi: [10.1016/j.solmat.2024.112863](https://doi.org/10.1016/j.solmat.2024.112863).
- I. García, M. Ghosh, **V. Orejuela**, P. Roca i Cabarrocas and, I. Rey-Stolle, “III-V Multijunction Solar Cells on Ultrathin Ge|si Virtual Substrates Grown at Low Temperature by RF-PECVD. doi: [10.4229/EUPVSEC20212021-3BO.10.2](https://doi.org/10.4229/EUPVSEC20212021-3BO.10.2).
- V. Depauw, C. Porret, M. Moelants, E. Veccio, K. Kennes, H. Han, R. Loo, J. Cho, G. Courtois, R. Kurstjens, K. Dessein, **V. Orejuela**, C. Sanchez-Perez, I. Rey-Stolle, and I. García, “Wafer-scale Ge epitaxial foils grown at high growth rates and released from porous substrates for triple-junction solar cells,” *Progress in Photovoltaics: Research and Applications*, vol. 31, no. 12, pp. 1315–1328, 2023, doi: [10.1002/pip.3634](https://doi.org/10.1002/pip.3634).

- A. Luque, P. Martín, R. Molinero, **V. Orejuela**, C. Sanchez-Perez, M. Zehender, I. García, I. Luque-Heredia and, I. Rey-Stolle, “Advanced Germanium TPV Cells for Latent Heat Thermal Batteries,” in *2023 IEEE 50th Photovoltaic Specialists Conference (PVSC)*, Jun. 2023, pp. 1–1. doi: [10.1109/PVSC48320.2023.10359958](https://doi.org/10.1109/PVSC48320.2023.10359958).
- I. Garcia, A. Cano, **V. Orejuela**, P. Martí, and I. Rey-Stolle, “Dense Array TPV Modules with Alternating Polarity InGaAs Cells,” Jun. 2023, pp. 1–3. doi: [10.1109/PVSC48320.2023.10359803](https://doi.org/10.1109/PVSC48320.2023.10359803).

Conferences

- Poster presentation at the 2021 13th Spanish Conference on Electron Devices (CDE) titled "[Advances in the Development of High Efficiency III-V Multijunction Solar Cells on Ge/Si Virtual Substrates](#)"
- Oral presentation at the European Materials Research Society (E-MRS) Spring 2023, titled "[Understanding the Effect of Cross Diffusion in GaAs/Ge Heterojunctions Grown by MOVPE on Photovoltaic Device Performance](#)"