Growth and Characterization of III-Phosphide Materials and Solar Cells for III-V/Si Photovoltaic Applications

Dissertation

Presented in Partial Fulfillment of the Requirements for the Degree
Doctor in Philosophy in the Graduate School of The Ohio State University

By

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2014

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Utilizing major advances in III-V/Si epitaxy is a promising approach to realize high-efficiency, cost efficient terrestrial solar power. The successful demonstration of planar GaP epitaxial layers free of nucleation-related defects grown on Si by both MBE and MOCVD establishes extremely fertile ground for the development of high quality III-V devices on Si substrates. Solar cell devices in particular stand to benefit, and not only by the merging of the best performing photovoltaic materials with the cost, availability, and scalability advantages of Si substrates, but also because of the advanced state of Si PV itself.

With this motivation in mind, several aspects of a III-V/Si multijunction solar cell are investigated in this dissertation. Such a device requires many advanced and novel components. The use of GaP as the bridge from Si to the wide range of III-V materials renews interest in a material whose activity in research efforts had faded significantly since the advent of modern growth techniques and GaAs-based heterostructures in the 1980s. GaP-based research is also motivated by the fact that it represents the far lesser studied binary component of both Ga_xIn_{1-x}P and GaAs_{1-y}P_{y}, two alloys essential to the wider scope of high efficiency PV research. Efforts to advance the ability to grow GaP by MBE and MOCVD were undertaken. Post-growth surface morphologies of homoepitaxial GaP films grown by MBE and MOCVD have been studied. Smooth, stepped surface morphologies of MBE-grown layers, measured by atomic force microscopy, were found for a wide range
of substrate temperatures and P$_2$:Ga flux ratios. A MOCVD-based growth study performed under similar conditions to MBE-grown samples show a nearly identical smooth, step-flow surface morphology, presenting a convergence of growth conditions for the two different methods. Electrical characterization of these films was then carried out by Hall effect measurements and DLTS to determine transport properties and to test for the presence of defect levels. Si-doped GaP showed mobilities that compare well to previous studies concerning n-type GaP grown by vapor- and liquid-phase growth methods. An activation energy greater than 80 meV, confirming the relatively deep position of the Si donor atom in these GaP films, was extracted from fits of temperature dependent Hall effect measurements, agreeing with similar measurements carried out several decades ago on vapor-phase grown samples. DLTS measurements revealed seven distinct majority-carrier deep levels for the films grown by MBE and current experiments to compare MBE and MOCVD films are discussed.

The other major material of interest in this work is Ga$_x$In$_{1-x}$P. A significant effort is currently being made throughout the PV area to develop high bandgap top junction subcells which are needed for a variety of technologies to continue to push the boundaries of high-efficiency solar cells. Ga-rich compositions of Ga$_x$In$_{1-x}$P are prime candidates that can achieve direct bandgaps of up to about 2.2 eV. Prototype Ga$_{0.57}$In$_{0.43}$P solar cells have been grown by MBE and MOCVD on GaAs$_y$P$_{1-y}$ compositionally graded buffers in order to optimize the cell structures, compare performance between the two growth methods, and to investigate the effects of threading dislocation density on solar cell performance metrics and material properties. Major improvements were made in the subcells by both growth techniques. The MOCVD-grown subcells, at this juncture, have shown superior
performance likely due to the greater degree of freedom in growth parameters, most notably the ability to grow at higher temperature to increase crystalline quality; a conclusion supported by the fact that post-growth annealing of the MBE-grown subcells resulted in better material properties as measured by photoluminescence as well as lower levels of depletion recombination current in the solar cell junction itself and better photovoltaic performance: larger $V_{OC}$ and FF. In addition to standard photovoltaic characterization methods, DLTS and DLOS were used to determine the presence of bandgap states in the MBE-grown solar cell devices and to observe their sensitivity to threading dislocation density. Three total majority carrier levels were found within the Ga$_{0.57}$In$_{0.43}$P bandgap, one by DLTS ($E_V + 0.70$ eV) and two by DLOS ($E_V + 0.90$ eV, $E_V + 1.82$ eV).

The results obtained during the course of this research present significant strides in the understanding of several challenging components essential to the development of a III-V/Si multijunction device. Experience gained for the growth and material properties of GaP epitaxial layers and for the development of high bandgap Ga$_x$In$_{1-x}$P solar cells are of interest to a wide range of semiconductor technologies. The comparison of the materials and devices between two of the most important and common modern semiconductor growth methods in both the research and commercial worlds expands the impact of the work.
To Mom and Dad,
Thank you for all that you’ve done for me.

To Kath, Alex and of course, Xavi,
Welcome to the world little dude!
Acknowledgements

I would first like to thank my advisor, Steve Ringel, for the opportunity to be a part of such a unique and strong research group that has evolved from his dedication and vision. I am extremely grateful to have received your support and guidance throughout my career as a graduate student in this group.

I am seriously indebted to all my coworkers over the years, without whom none of this work would have been possible. To Tyler Grassman, who really taught me what it takes to be a serious and dedicated scientist. Your example in performing creative, impactful, and thorough research will surely stick with me as an example for all of my professional life. To Mark Brenner, for all his hard work that has enabled my research in the lab. For working with me to solve my problems and helping me to understand all the systems. And for being an awesome guy and for all the laughs. To Aaron Arehart for always being ready and willing to share his knowledge and experience. To Andrew Carlin, for all the hours working side-by-side, teaching me how to run experiments, fix equipment, and work with samples. To Dan, your curiosity and drive have helped me to continue learning and crystallizing ideas in my mind as well as to keep my perspective fresh. To Pran for all your hard work over the last year or so working on a difficult experiment and staying positive and being a joy to work with. And to the rest of the MBE/solar family: Austin, Deep, Drew, Krishna, and Nathan – wouldn’t have been the same without you guys.
Most importantly, I would like to thank my family and friends for all their support throughout my life. My parents for their unwavering support for me and my education. I love you guys and feel so fortunate to have such awesome parents who have guided me to such a good place in life. To Kath, for your unwavering support of, and dedication to, Nelson. What can I say, you learn so much from an older sister. Seeing the world through your eyes and all that you’ve shown me and introduced me to has had an enormous impact on who I am today. I can’t wait for all the good times we will have as a family in the future.

To Ben and Briana, your house was my sanctuary of peace and fun for many years and Columbus was not the same when you left. To Maria, I’m truly thankful for the experiences we shared, which mean so much to me, thank you for all of your support. To Javier, it was great to get to know you and whether you’re working on research or cruising southern Europe by moto I wish you the best. To Joe, Tim, Jeremy, Judith, Mike, Geoff, Ryan, Matt, Zach, Mark, Jon, Ben, Santa Maria, and the entire Columbus ultimate community. You guys have made my life so fun in my time here in Columbus. And finally, to Janine, I can’t express how glad I’ve been to have you as a part of my life these last couple years. You are one of the best people I’ve ever known and your friendship and support have enriched my life profoundly.
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<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BSF</td>
<td>Back Surface Field</td>
</tr>
<tr>
<td>CM</td>
<td>Composition Modulation</td>
</tr>
<tr>
<td>CuPt</td>
<td>Copper Platinum</td>
</tr>
<tr>
<td>DIV</td>
<td>Dark Current-Voltage</td>
</tr>
<tr>
<td>DLOS</td>
<td>Deep Level Optical Spectroscopy</td>
</tr>
<tr>
<td>DLTS</td>
<td>Deep Level Transient Spectroscopy</td>
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<tr>
<td>EBIC</td>
<td>Electron Beam Induced Current</td>
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<tr>
<td>EQE</td>
<td>External Quantum Efficiency</td>
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<tr>
<td>FF</td>
<td>Fill Factor</td>
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<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
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<tr>
<td>GaAsP</td>
<td>Gallium Arsenide Phosphide</td>
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<tr>
<td>GaP</td>
<td>Gallium Phosphide</td>
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<tr>
<td>GaInP</td>
<td>Gallium Indium Phosphide</td>
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<tr>
<td>HRXRD</td>
<td>High-Resolution X-Ray Diffraction</td>
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<tr>
<td>JSC</td>
<td>Short Circuit Current Density</td>
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<tr>
<td>IQE</td>
<td>Internal Quantum Efficiency</td>
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<td>LIV</td>
<td>Lighted Current Voltage</td>
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<td>LPE</td>
<td>Liquid Phase Epitaxy</td>
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<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
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<tr>
<td>MJ</td>
<td>Multijunction</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal-Organic Chemical Vapor Deposition</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<td>PV</td>
<td>photovoltaics</td>
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<td>Reflection</td>
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<tr>
<td>RHEED</td>
<td>Reflection High Energy Electron Diffraction</td>
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<td>Steady State Photocapacitance</td>
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<tr>
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<td>Threading Dislocation Density</td>
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<td>Transmission Electron Microscopy</td>
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<tr>
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<td>Open-circuit voltage</td>
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<td>Vapor Phase Epitaxy</td>
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<tr>
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Chapter 1

Introduction

III-V multijunction solar cells are the highest performing photovoltaic technology available today and have been for many years since early progress toward high quality Ga$_{0.51}$In$_{0.49}$P/GaAs tandem cells which were able to exceed efficiencies of 30% [1-3]. Modern multijunction solar cells are pushing efficiencies well into the 40% range [4]. With recent breakthroughs in the decades-old goal of integrating III-V materials with Si substrates [5, 6], the potential for III-V/Si photovoltaics to present a paradigm shift in the use of high-efficiency solar materials for terrestrial purposes is closer to becoming a reality. Beyond leveraging the lower cost, greater abundance, and highly advanced, world-wide manufacturing base, Si affords the unique advantage that it itself is an advanced photovoltaic material, and itself can be used as an active photovoltaic junction within a III-V/Si multijunction cell. Among the challenges introduced by the combining of these technologies is the need for advancements in the growth and characterization of large bandgap III-phosphide compound semiconductors: (1) GaP, which is both the critical epitaxial nucleation layer between the Si substrate/sub-cell and the III-V sub-cells as well as the binary constituent of the critical GaAs$_y$P$_{1-y}$ and Ga$_x$In$_{1-x}$P materials that comprise the
III-V part of the III-V/Si multijunction, and (2) novel compositions of GaIn_{1-x}P as the top junction subcell. These subjects are the focus of this dissertation.

1.1 Motivation for Solar Research

The most recent report issued by the International Panel on Climate Change (IPCC) has given dire warnings regarding anthropogenic climate change in the 21st century [7]. Energy demand worldwide is rapidly increasing due to growth in population and economic activity. Limits suggested by the IPCC report concerning the amount of fossil fuels that may be exploited before irreversible climate disaster are far less than the predicted quantities of these fuels still in the ground. With the apparent inability of current global socio-economic structures to deal with this problem, despite the fact that renewable energy sources have proven their merit [8], the continued development of clean and safe renewable energy sources is more important than ever to obtain further economic advantages.

Solar cells today are finding increased application in terrestrial energy systems, from roof-mounted installations on houses that are either on or off the power grid, to small-scale systems such as remote power supplies for communication and monitoring systems, to large scale, primary grid integrated arrays. Indeed, research into the use of photovoltaic (PV) systems for large-scale power generation has now been ongoing for several decades [9]. But despite being a clean and abundant energy source and despite extremely rapid relative growth of total annual PV shipments (approximately 25%/year) compared to all other forms of energy supply, the successful market penetration of large scale terrestrial solar power based on conventional PV technology still requires further reductions in production costs at scale relative to other forms of energy production. Today energy production from solar panels represents less than 1% of total United States energy
production [10]. Reduction in cost is therefore the major motivation in terrestrial photovoltaic research and can be achieved through innovations in manufacturing methods, solar cell modules, and the photovoltaic devices themselves.

1.2 **High Efficiency III-V Solar Cells**

There are essentially two strategies for large scale terrestrial photovoltaic power generation: flat plate systems and concentrator systems. Flat plate systems are large area modules of cheaper, lower efficiency devices. Concentrator systems utilize concentrated sunlight on small area, high efficiency cells. High efficiency solar cells were originally developed as a power source for satellites and today are the dominant technology for space photovoltaic application where efficiency, size, radiation hardness, material weight, and end-of-life performance are the priorities and cost (at the cell level) is secondary due to larger cost reductions at the system level enabled by the high efficiency cell. The highest efficiency solar cells today are based on III-V materials which allow for multijunction cells that can be better utilized to match the sun’s solar spectrum compared with single junction technologies and therefore result in higher efficiency energy converters. The monolithic integration of different high efficiency materials with different band gaps to achieve even better (and broader) spectral utilization has allowed for solar cell efficiencies of over 40% under concentration [4, 11]. The current world record efficiency is 44.7% (at 297 suns), held by a four junction III-V cell whose one-sun lighted current-voltage curve (LIV) is shown in Figure 1.1 [4]. The high cost of high-efficiency III-V devices, however, has impacted their acceptance as a viable terrestrial energy option in spite of their superior performance to every other photovoltaic material. The question, therefore, is how to use high-efficiency III-V solar technology to reduce the cost of terrestrial PV?
Figure 1.1: Demonstrated lighted current-voltage (LIV) curve for world record, 44.7% efficient III-V four-junction solar cell shown here under 1 sun AM1.5D solar spectrum [4]. The world record efficiency value is for the same cell under 297 sun concentration.

1.3 **Substrates for III-V PV**

The high costs are due in large part to the cost of conventional GaAs or Ge substrates, which have been historically chosen since they provide a good lattice match for subsequent GaAs-based epitaxy. This has resulted in a tremendous interest in replacing conventional substrates for III-V technologies with a low-cost alternative substrate – for example, Si. Silicon possesses enormous advantages for III-V based PV technologies: (1) Si electronics are among the world’s largest manufacturing industries, and as a result large area Si substrates are very inexpensive, readily available at extraordinary scale and their
development does not require massive capital expenditures; (2) compared with Ge or GaAs, Si possesses far superior substrate properties with respect to mass density, mechanical strength and thermal conductivity; (3) Si is the second most abundant element on Earth; and (4) Si itself is already an outstanding PV device technology in terms of performance, with crystalline silicon cells reaching efficiencies of 25% [12]. These facts, coupled with the realization that specific III-V materials can enable integration of III-V solar cells with Si via the use of a semi-transparent, GaAs$_y$P$_{1-y}$, buffer layer, reveal an extremely promising potential solar cell structure in which the Si substrate itself can also be incorporated as an active sub-cell to create a III-V/active-Si device architecture.

1.4 **Motivation and Research Objectives**

Gallium phosphide (GaP), which, while receiving widespread interest in the 1960s and 1970s for its use as a material for light emitting diodes (LEDs) based on bulk substrates and early epitaxy methods like chloride vapor phase epitaxy, has garnered few efforts in the era of MOCVD and MBE-dominated semiconductor growth techniques that are far superior to their predecessors. These methods have enabled all forms of quantum well and superlattice-based optoelectronic devices using III-V semiconductors such as GaAs, Al$_x$Ga$_{1-x}$As, InP, Ga$_x$In$_{1-x}$P, etc, that rendered GaP, with its indirect bandgap, to be of little to no interest for LED applications since the 1970’s. In addition, MBE and in particular MOCVD, are the epitaxy growth methods of choice for all III-V solar cells. As a result, there is both a glaring omission of and need for information regarding both MOCVD and MBE growth of GaP in general, and of MBE and MOCVD growth of GaP on Si in particular. As will be seen in this dissertation, not only is such information necessary to grow ideal, planar GaP on Si, but it is also necessary to optimize growth of unusual, Ga-
rich compositions of the Ga\textsubscript{x}In\textsubscript{1-x}P and GaAs\textsubscript{y}P\textsubscript{1-y} alloy systems that are needed to create an optimum solar cell structure that combines III-V cells with Si cells in an all-epitaxial format. Investigations into the growth and characterization of GaP layers grown by MBE and MOCVD are a major objective of this thesis.

Among the III-V materials widely used in optoelectronic devices, the ternary alloy Ga\textsubscript{x}In\textsubscript{1-x}P has proven to be indispensable. Ga\textsubscript{x}In\textsubscript{1-x}P alloys with compositions of x = 0.51 are a mainstay of several device technologies since it is lattice matched with GaAs and its relatively large bandgap (1.9 eV without lattice ordering) and electron affinity difference with respect to GaAs create type I heterojunctions (with $\Delta E_C = 0.2$ eV, $\Delta E_V = 0.28$ eV) for both n and p type doping. Hence, Ga\textsubscript{0.51}In\textsubscript{0.49}P/GaAs heterojunctions, quantum wells and superlattices are used as the key components of III-V heterojunction bipolar transistors (HBTs), red visible LEDs and laser diodes, various photodetectors, and, as described earlier, III-V solar cells [2, 14, 15]. Additionally, from a technological perspective Ga\textsubscript{0.51}In\textsubscript{0.49}P has an important advantage over Al\textsubscript{x}Ga\textsubscript{1-x}As as a lattice-matched wide bandgap partner with GaAs since the avoidance of Al in Ga\textsubscript{0.51}In\textsubscript{0.49}P epitaxy greatly reduces unwanted oxygen incorporation in the material.

As will be shown in Chapter 2, a multijunction solar cell based on a Si subcell require middle and top junctions of bandgaps different from the standard technologies utilized today. The top junction, in particular, requires a direct bandgap of between 1.95 and 2.05 eV, depending on the solar spectrum available. It turns out that direct bandgaps above 1.90 eV at room temperature (the bandgap of completely disordered Ga\textsubscript{0.51}In\textsubscript{0.49}P lattice matched to GaAs) are not straightforward and rare in current solar cell designs. Unusual compositions of the Ga\textsubscript{x}In\textsubscript{1-x}P alloy are able to provide larger bandgaps.
Development of a Ga-rich Ga\textsubscript{x}In\textsubscript{1-x}P top cell technology that meets the necessary bandgap values, from epitaxy through PV devices, is another major objective of this thesis.

Finally, it is of interest to be able to work with these materials systems in both the MBE and MOCVD environments. Both growth methods can provide high throughput, but the MOCVD system has traditionally been the more commercially-relevant growth system, particularly for III-V multijunctions, in part due to relative ease of scaling to large area substrates [16]. Additionally, although high quality Ga\textsubscript{x}In\textsubscript{1-x}P devices can be created in either growth system, it is well known that the MOCVD growth environment affords considerably greater flexibility in Ga\textsubscript{x}In\textsubscript{1-x}P growth conditions which in turn allows for greater control of its material properties and reduction of crystal defect concentrations. While MBE was the primary growth system used, efforts toward understanding MOCVD growth and comparisons between MOCVD- and MBE-grown films were pursued throughout this work since this provides a way to explore the influence of very large ranges of growth conditions on the properties and quality of the epitaxial materials.

1.5 Synopsis

This thesis is organized as follows. Chapters 2 and 3 focus on background necessary to the discussion of the results of this work. In Chapter 2, multijunction solar cell device physics and the III-V/Si-subcell device are presented in detail. In Chapter 3, epitaxial challenges resultant from the III-V/Si multijunction solar cell including III-V/IV growth, metamorphic buffers, and Ga\textsubscript{x}In\textsubscript{1-x}P epitaxy are discussed. In Chapter 4 the experimental techniques used in this thesis are described in detail.

Chapter 5 presents work done on GaP. A novel, high temperature growth regime for MBE-GaP was discovered in the course of this work where a step-flow growth mode
with atomically-smooth surfaces is revealed. Electrical characterization of these layers, including temperature dependent Hall effect and Deep Level Transient Spectroscopy (DLTS) were also performed. This growth space was found to correspond closely in growth conditions and surface morphology to films grown by MOCVD, identifying an unusual crossover point between the two growth methods.

Chapter 6 presents work done on Ga$_{0.57}$In$_{0.43}$P single junction solar cells grown by MBE. Growth conditions are briefly verified (phosphides and indium-containing materials have been grown extensively in this group in the past) prior to the growth and fabrication of a series of single junction cells to test effects of different cell component layers, such as back surface field (BSF) and window layers. In order to determine the effects of threading dislocation density (TDD), results from a single junction solar cell grown on substrate/graded buffer combinations of widely varying TDD are presented. These cell structures are then subjected to measurement by DLTS and Deep Level Optical Spectroscopy (DLOS) to determine to what extent existing trap levels are exacerbated by the increased TDD. Efforts toward developing high bandgap single junction Ga$_{0.57}$In$_{0.43}$P cells in the MOCVD growth environment are described in Chapter 7. In Chapter 8, the results are summarized and the future work is discussed.

1.6 References


Chapter 2

Fundamentals of Multijunction Solar Cells

This chapter describes the physics, design, and operation of multijunction solar cells in order to provide a foundation to facilitate the discussion of data and results in terms of the long-term goal of this work: a Si-based multijunction solar cell. As discussed in Chapter 1, multijunction solar cells are able to achieve significantly higher efficiencies than single junctions due to better spectral utilization. This idea is expounded in this chapter with regard to the Si-based device of interest. It will be shown that the ideal Si-based multijunction solar cell requires a shift in lattice constant between the different subcells which in turn involves the introduction of crystalline defects known as threading dislocations. Fundamental equations describing the function of solar cells will be introduced in order to demonstrate the effect of threading dislocations on solar performance.

2.1 Solar Spectrum

The first topic that must be discussed is the energy source provided. The spectrum of energy from the sun varies greatly depending on a number of factors such as local variations in atmosphere and weather, the latitude, the season of the year, etc. The three
standard spectra generally used in solar research are plotted in Figure 2.1. AM0 is the solar spectrum outside the Earth’s atmosphere and is used for space applications, AM1.5G is the standard spectrum at the Earth’s surface for both direct and diffuse radiation and is used for terrestrial flat-panel, and AM1.5D is the standard spectrum at the Earth’s surface for only direct radiation and is used for concentrator solar cells. The difference in the spectra comes down to the atmosphere’s interference with the solar radiation. Reflection, scattering, and absorption all play a role. The dips in the AM1.5G and AM1.5D spectra are due to especially strong absorption of certain wavelengths of light by molecules in the atmosphere such as CO₂, H₂O vapor, and ozone (O₃). As mentioned in the introduction, this work is ultimately motivated by decreasing costs of terrestrial-based solar energy production. As such, the solar cell measurements discussed in this dissertation are measured with respect to the AM1.5G solar spectrum.
2.2 Multijunction Solar Cells

Single junction solar cells are limited in their ultimate efficiency. A single crystal semiconductor is transparent to photons with energy below its bandgap. Photons with energy greater than the bandgap of the semiconductor experience energy loss in the form of thermalization; excited electrons relax to the conduction band minimum, releasing the excess energy as heat. This trade-off between collecting a greater number of photons and
using collected photons efficiently can be appeased through the use of multijunction solar cells. By stacking photovoltaic junctions on top of one another in series, as in Figure 2.2 (a), the solar spectrum can be partitioned (Figure 2.2 (b)), reducing thermalization loss while increasing the total amount of energy absorbed from the sun.

Figure 2.2: The benefits of multijunction solar cells are shown in (a) where light from the sun is picked off by subsequent junctions of the solar cell stack, according to the bandgap of each junction. The AM1.5G solar spectrum is shown in (b) partitioned by the wavelengths corresponding to the bandgaps of the Ga$_{0.57}$In$_{0.43}$P/GaAs$_{0.90}$P$_{0.10}$/Si multijunction solar cell of interest in this work.
2.2.1 Conversion Efficiencies

The trade-off between thermalization loss and photon absorption is expressed in Figure 2.3 where maximum efficiencies for a single junction solar cell of varying bandgap are plotted [2]. These efficiencies are calculated for several situations using the Shockley-Queisser detailed balance model [3]. This approach, originally presented in 1961, considered the sun and the solar cell as black bodies with the solar cell collecting all light above its bandgap. By using Planck’s law to calculate the photon flux coming from the sun (a black body of 6000 K) with energy above a given bandgap, an ideal, ultimate efficiency is found at about 45% for a bandgap of around 1.1 eV. This is shown as the “ultimate efficiency” curve of Figure 2.3. The ultimate efficiency assumes a photon impingement from all sides and a perfect, lossless absorber. For a more realistic picture, photon flux from the sun is limited to a finite angle and losses are allowed in the semiconductor by modeling the solar cell as a black body with temperature of 300 K in thermodynamic equilibrium with its ambient surroundings so that it must emit, as well as absorb, radiation. This radiative emission essentially provides the $J_0$ term of the standard solar cell equation which can be used to calculate efficiency. The photocurrent enters through the summed flux impinging on the cell given a bandgap and that each photon is absorbed and excites a carrier with energy equal to the bandgap. The rectifier term follows from the proportionality of radiative recombination to the np product and its dependence on the splitting of the quasi-Fermi levels. By this method an estimation for efficiency that is independent of material and design is obtained. This “radiative limit” estimation results in a maximum conversion efficiency of about 30%, the well-known Shockley-Queisser limit for a single junction solar cell.
2.2.2 III-V/Si MJ Solar Cell

This same formulation can be used to estimate the maximum efficiency of a multijunction solar cell given a set of bandgaps and simply summing the I-V equation from each junction. This was done to determine the optimal bandgaps for a triple junction solar cell based on a Si-subcell under three different solar spectra. The results are shown in the iso-efficiency contour plots of Figure 2.4 where the x and y axes represent the bandgaps of the middle and top junctions, respectively.
Figure 2.4: Iso-efficiency contour plots depicting ideal middle and top cell bandgap ranges given a 1.12 eV bottom junction for AM0 (a), AM1.5G (b) and 100X concentrated AM1.5D spectra (c).

The calculations of Figure 2.4 show the ideal band gaps for the triple junction solar cell of interest. For the terrestrial spectra, they show bandgap values to be in the range of 1.45 – 1.55 eV for the second junction and 1.95 – 2.05 eV for the top cell assuming a bottom junction consisting of Si with a bandgap of 1.12 eV. This directly demonstrates one of the primary motivations of this dissertation: the need for a high bandgap top junction.
The ability to choose bandgaps is part of what makes III-V materials so powerful for PV applications. Since a given III-V semiconductor is associated with both a characteristic lattice constant as well as a bandgap, the freedom of bandgap choice requires changes in lattice constant. The epitaxy of lattice mismatched materials, known as metamorphic growth, is a critical part of modern semiconductor engineering. The well-known lattice constant vs. bandgap map is shown in Figure 2.5 for the As and P containing III-V materials as well as the group IV materials Si and Ge. The tie lines represent the bandgap values for the alloy systems, such as Ga_xIn_{1-x}P where the bandgap values correspond to a given lattice constant between InP and GaP. The dashed tie lines represent the compositional ranges of the alloy where its minimum bandgap is indirect in nature, and the solid lines represent compositions for which the bandgap is direct in nature and thus ideal for optoelectronic and solar cell applications. The shaded horizontal bars represent the ideal bandgaps for a triple junction cell, as determined from the calculations of Figure 2.4. It is obvious then that the optimal bandgaps derived for a triple junction solar cell including Si cannot be achieved at a single lattice constant. The solution is to change the lattice constant and this requires lattice-mismatched metamorphic epitaxy.

The strategy for creating the desired structure is shown by the arrows and circles of Figure 2.5. By beginning with a Si subcell/substrate with a GaP nucleation layer, the lattice constant must be increased in order to reach the desired bandgaps of the subsequent layers. The use of a GaAs_yP_{1-y} step-graded buffer facilitates the required lattice constant change while maintaining a bandgap above that of the overlying middle and top III-V sub-cell bandgaps, which is necessary to allow maximum optical access to the Si subcell as it creates an effective “transparent” graded buffer. Grown above (on top of) the graded GaAs_yP_{1-y}
buffer, GaAs$_{0.90}$P$_{0.10}$ provides a bandgap of about 1.55 eV for the middle junction, upon which an internally lattice-matched (to the GaAs$_{0.90}$P$_{0.10}$ middle junction) top cell with a composition of Ga$_{0.57}$In$_{0.43}$P can be grown, which possesses a direct bandgap of approximately 1.95 eV. The details of this methodology, including background on GaP/Si growth and metamorphic step-graded buffers, are described in detail in Chapter 3.

Figure 2.5: Lattice constant versus bandgap map with horizontal shaded bars showing optimal bandgap splits under AM1.5G illumination for a Si subcell-based triple junction solar cell. Arrows and circles representing the growth methodology and target lattice constants.
Figure 2.6: Schematic diagram showing a possible structure for the three junction, n\textsuperscript+p solar cell device on Si following the strategy outlined in Figure 2.5 with the all-important GaP/Si nucleation layer, two GaAs\textsubscript{0.90}P\textsubscript{0.10} tunnel junctions, and the Ga\textsubscript{0.57}In\textsubscript{0.43}P, GaAs\textsubscript{0.90}P\textsubscript{0.10}, and Si subcells complete with BSF and window layers. Bandgap values for each material and realistic values for layer thicknesses are given.

<table>
<thead>
<tr>
<th>Top Subcell</th>
<th>Material</th>
<th>Bandgap (eV)</th>
<th>Thickness (μm)</th>
</tr>
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<td>Top contact</td>
<td>Ni/Ge/Au</td>
<td>1.50</td>
<td>0.3</td>
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<td>0.3</td>
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<td>0.05</td>
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<td>1.95</td>
<td>0.5</td>
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<td>Back-surface field (p\textsuperscript{+})</td>
<td>(Al\textsubscript{0.5}Ga\textsubscript{0.43})\textsubscript{0.5}In\textsubscript{0.43}P</td>
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<td>0.03</td>
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</tr>
<tr>
<td>Emitter (n\textsuperscript{+})</td>
<td>GaAs\textsubscript{0.90}P\textsubscript{0.10}</td>
<td>1.50</td>
<td>0.05</td>
</tr>
<tr>
<td>Base (p)</td>
<td>GaAs\textsubscript{0.90}P\textsubscript{0.10}</td>
<td>1.50</td>
<td>1.0</td>
</tr>
<tr>
<td>Back-surface field (p\textsuperscript{+})</td>
<td>(Al\textsubscript{0.5}Ga\textsubscript{0.43})As\textsubscript{0.5}P</td>
<td>1.3</td>
<td>0.03</td>
</tr>
<tr>
<td>Tunnel Junction</td>
<td>p\textsuperscript{++}</td>
<td>GaAs\textsubscript{0.90}P\textsubscript{0.10}</td>
<td>1.50</td>
</tr>
<tr>
<td>n\textsuperscript{++}</td>
<td>GaAs\textsubscript{0.90}P\textsubscript{0.10}</td>
<td>1.50</td>
<td>0.02</td>
</tr>
<tr>
<td>Graded Buffer</td>
<td>GaP → GaAs\textsubscript{0.9}P\textsubscript{0.1} (n\textsuperscript{+})</td>
<td>GaAs\textsubscript{0.9}P\textsubscript{1-y}</td>
<td>2.26 → 1.55</td>
</tr>
<tr>
<td></td>
<td>GaP (n\textsuperscript{+})</td>
<td>GaP</td>
<td>2.26</td>
</tr>
<tr>
<td>Window (n\textsuperscript{+})</td>
<td>GaP</td>
<td>2.26</td>
<td>0.01</td>
</tr>
<tr>
<td>Emitter (n\textsuperscript{+})</td>
<td>Si</td>
<td>1.12</td>
<td>0.03</td>
</tr>
<tr>
<td>Base (p)</td>
<td>Si</td>
<td>1.12</td>
<td>--</td>
</tr>
</tbody>
</table>

To show this more clearly, Figure 2.6 represents a possible structure that achieves the strategy expressed in Figure 2.5. It also illustrates the numerous fascinating research challenges that are involved with this goal: GaP/Si nucleation, GaAs\textsubscript{y}P\textsubscript{1-y} step-graded buffers (SGBs), novel compositions of GaAs\textsubscript{y}P\textsubscript{1-y} and Ga\textsubscript{a}In\textsubscript{1-x}P for subcells and tunnel junctions, and subcell passivation layers. Each of these components will be discussed in
detail in the following pages of this dissertation. The zero-bias band diagram corresponding to this structure is shown in Figure 2.8.

2.2.3 Multijunction I-V Characteristics

Changing the lattice constant in this way necessarily involves the introduction of crystalline defects, most notably threading dislocations. Dislocations play a dominant role in the photovoltaic properties of metamorphic multijunction solar cells. While the physical nature of threading dislocations and their control and mitigation through epitaxy are described in Chapter 3, here some basic PV equations are given both to aid in setting up the framework for discussions on the components of multijunction solar cells as well as to demonstrate the effect of threading dislocations on photovoltaic performance. The basic ideal solar cell diode equation (no parasitics, superposition of light generated current with the ideal diode is assumed, for now) is given by Equation 2.1:

\[ J = J_0 \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) - J_L \]  

Equation 2.1

Where \( J \) is current density, \( J_0 \) is reverse saturation current density, \( q \) is the electronic charge, \( V \) is voltage, \( k \) is Boltzmann’s constant, \( T \) is temperature and \( J_L \) is the photogenerated current. The parameters used to measure the efficiency (Equation 2.2) of a solar cell are the open-circuit voltage (\( V_{OC} \)), the fill factor (\( FF \), Eq. 2.3) and the short circuit current density (\( J_{SC} \)).

\[ \eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \]  

Equation 2.2

Where \( P_{in} \) is the incident photon energy per area. \( FF \) is defined by:

\[ FF = \frac{J_{MP} \times V_{MP}}{J_{SC} \times V_{OC}} \]  

Equation 2.3
Where J_{MP} and V_{MP} represent the coordinates of the maximum power point of the LIV curve, where J \times V is a maximum. FF is a measure of the “squareness” of the IV curve. Open circuit voltage can be defined as:

\[
V_{OC} = \frac{n k T}{q} \ln \left( \frac{J_L}{J_0} + 1 \right)
\]

Equation 2.4

Equation 2.4 is simply the rearranged version of the diode equation when J = 0. It shows that V_{OC} is dependent on J_L and J_0. Of these two parameters, J_0 is the more significant since it can vary by orders of magnitude. Two contributions to J_0 are generally considered: J_{01}, the ideal diode diffusion component current and J_{02}, the depletion region recombination current. The full diode equation thus becomes:

\[
J = J_{01} \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) + J_{02} \left( \exp \left( \frac{qV}{2kT} \right) - 1 \right) - J_L
\]

Equation 2.5

Where J_{01} is calculated from a combined contribution of each side of the p-n junction:

\[
J_{01} = J_p + J_n
\]

\[
= q n_i^2 \left( \frac{F_p}{N_A} \left( \frac{D_n}{\tau_n} \right)^{1/2} + \frac{F_n}{N_D} \left( \frac{D_p}{\tau_p} \right)^{1/2} \right)
\]

Equation 2.6

Where:

\[
F_p = \frac{S_n \cosh \left( \frac{W_p}{L_n} \right) + \left( \frac{D_n}{L_n} \right) \sinh \left( \frac{W_p}{L_n} \right)}{S_n \sinh \left( \frac{W_p}{L_n} \right) + \left( \frac{D_n}{L_n} \right) \cosh \left( \frac{W_p}{L_n} \right)}
\]

\[
F_n = \frac{S_p \cosh \left( \frac{W_n}{L_p} \right) + \left( \frac{D_p}{L_p} \right) \sinh \left( \frac{W_n}{L_p} \right)}{S_p \sinh \left( \frac{W_n}{L_p} \right) + \left( \frac{D_p}{L_p} \right) \cosh \left( \frac{W_n}{L_p} \right)}
\]
From this expression we see that $J_{01}$ is determined by the design of a diode as well as the properties of the material in question. This expression is derived assuming no recombination in the depletion region of the diode. The purpose of the $J_{02}$ term is to include the depletion region recombination. The $J_{02}$ contribution therefore becomes very important for the understanding of how TDD affects a solar cell; it is the dominant dark current component for high levels of TDD. $J_{02}$, as derived from Shockley-Read-Hall statistics, is defined by:

$$J_{02} = qw_D \frac{n_i}{2\tau}$$  \hspace{1cm} \text{Equation 2.7}

In this expression, $w_D$ is the total depletion layer width and the lifetime, $\tau$, is a mixed contribution between the maximum lifetime ($\tau_{\text{max}}$) and the dislocation mediated lifetime ($\tau_{\text{TDD}}$):

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{max}}} + \frac{1}{\tau_{\text{TDD}}}$$  \hspace{1cm} \text{Equation 2.8}

In a semiconductor at a given doping concentration, the maximum lifetime includes all contributions in the absence of threading dislocations, i.e. Shockley-Read-Hall, Auger,
band-to-band, etc. The threading dislocation mediated lifetime can be calculated as in Yamaguchi et al. [4] by solving the one-dimensional diffusion equation for a carrier diffusing to and recombining at a dislocation.

\[ \frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \]  

Equation 2.9

The dislocation’s volume, which provides the boundary condition, in space is given as:

\[ \pi x_c^2 = \frac{1}{[TDD]} \]  

Equation 2.10

Where \( x_c \) is the unit cell radius of the dislocation core and \([TDD]\) is the density of dislocations. The solution results in a dislocation mediated diffusion length, \( L_{TDD} \) of:

\[ L_{TDD} = \frac{2}{\pi^{3/2} D [TDD]^{1/2}} \]  

Equation 2.11

Which, through the Einstein relation, \( L = \sqrt{\tau D} \), results in dislocation mediated lifetime:

\[ \tau_{TDD} = \frac{4}{\pi^3 D [TDD]} \]  

Equation 2.12

From these equations we see the inverse relationship between threading dislocation density and lifetime. Using this model one can therefore calculate the effect of TDD on a solar cell’s efficiency and parameters. This was done by Yamaguchi et al. for an n’p GaAs [5] solar cell whose conclusions are reproduced in Figure 2.7. It shows that for TDD above around \( 10^5 \text{ cm}^{-2} \) the performance of a GaAs solar cell decreases rapidly. The threshold is material dependent. Also, the effect of TDD on \( J_{SC} \) depends on the diffusion length relative to the thickness of the solar cell. If the diffusion length is greater than the base of the cell,
no significant change in $J_{SC}$ will be observed. $V_{OC}$ is therefore a better measure of the effect of TDD on a solar cell performance.

Figure 2.7: Plot of the calculated effect of threading dislocation on the major solar cell parameters for an n’p GaAs solar cell [5].

### 2.2.4 Bandgap-Open Circuit Voltage Offset ($W_{OC}$)

A very useful parameter to gauge the quality of a solar cell device with respect to material quality is the bandgap-open circuit voltage offset, $W_{OC}$, defined as $(E_g/q) - V_{OC}$. The utility of $W_{OC}$ derives from its ability to relate solar cells of widely different materials and bandgaps and as such is becoming increasingly used for metamorphic materials and multijunction solar cells [6-8]. This can be understood through the fundamental diode equations described above. From Equations 2.4 and 2.6, the dependence of $J_0$ and therefore $V_{OC}$ on $n_i^2$ is clear and thus the relation between $V_{OC}$ and bandgap. Following the
methodology used in Reference [6], an equation for $W_{OC}$ can be determined starting from its basic definition and Equation 2.4:

$$W_{OC} = \left(\frac{E_g}{q}\right) - V_{OC} = \left(\frac{E_g}{q}\right) - \frac{kT}{q} \ln\left(\frac{J_L}{J_0}\right) \quad \text{Equation 2.13}$$

Often simplifying assumptions are made for $J_0$ in

$$J_0 = q n_i^2 \left(\frac{F_p}{N_A} \left(\frac{D_n}{\tau_n}\right)^{1/2}\right) \quad \text{Equation 2.6}$$

the infinite diode approximation allows for $F_n = F_p = 1$ and the one-sided diode equation, in which only the p-side of an n$^+$p diode [9], with dopant concentration $N_A$, is considered, results in the following expression for $V_{OC}$:

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{J_L \tau N_A}{q w_p n_i^2}\right) \quad \text{Equation 2.14}$$

Where, if the radiative recombination limit is taken,

$$\tau = \frac{1}{B N_A} \quad \text{Equation 2.15}$$

Where $B$ is the radiative recombination coefficient for a given material. The bandgap dependence through $n_i^2$ in Equation 2.14 can be largely removed using the equation for $n_i$:

$$n_i^2 = N_v N_c \exp\left(-\frac{E_g}{kT}\right) \quad \text{Equation 2.16}$$

Such that:

$$V_{OC} = \left(\frac{E_g}{q}\right) - W_{OC} = \left(\frac{E_g}{q}\right) - \frac{kT}{q} \ln\left(\frac{q w B N_c N_v}{J_L}\right) \quad \text{Equation 2.17}$$

So that the resulting equation for $W_{OC}$ is:
\[ W_{OC} = \frac{kT}{q} \ln \left( \frac{q w B N_C N_V}{J_L} \right) \]  

Equation 2.18

Since the parameters here are only somewhat dependent on bandgap and device design \((N_C, N_V, w, J_L)\) and appear in the logarithmic term of this equation, \(W_{OC}\) is fairly constant across a wide range of bandgaps and so, generally speaking, a \(W_{OC}\) of about 0.4 V (it can be lower) is the best that can be achieved in the radiative limit, when all non-fundamental recombination mechanisms are reduced to zero [6].

2.2.5 Multijunction Cell Design Considerations

There are additional requirements for the fabrication of multijunction solar cells compared to single junctions. If the separate junctions are to be stacked monolithically in series with one another (the preferred setup), all the subcells must be closely current matched to one another. Since each subcell creates its own photogenerated current based on many factors, such as the portion of the spectrum it absorbs, the cell thickness, and the diffusion length of the material, there are different ways to achieve current matching such as bandgap selection and junction thinning. This is a critical part of multijunction design since the subcell that produces the least current will limit the entire device.

Control of parasitic resistance effects are also a top priority. Series and shunt resistances were neglected in Equation 2.1 but are included here:

\[ J = \frac{V + J_RS}{R_P} + J_0 \left( \exp \left( \frac{qV}{kT} \right) - 1 \right) - J_L \]  

Equation 2.19

Where \(R_S\) is series resistance and \(R_P\) is shunt resistance. Series resistance is generally the more difficult to control, especially for multijunction solar cells under concentration. This is due, in part, to the need for low resistance electrical interconnects to
switch polarity between the different junctions, since a series-integrated multijunction solar cell is really just a stack of opposing back-to-back diodes. This is generally provided by tunnel junction diodes which are heavily doped, extremely thin p-n junctions whose band structure results in filled electron states on the n-type side aligning with empty hole states on the p-type side separated only by a very thin barrier so that tunneling can occur. When properly designed, these interconnects can have very small voltage drops even up to very high current densities. The realization of good, low resistance tunnel junctions becomes more difficult for devices made with materials of larger bandgaps. They are necessary, however, if parasitic light absorption detrimental to subcells below is to be avoided. This is shown in the band diagram of Figure 2.8 which was calculated following the structure of the three junction, \( n^+p \) III-V/Si solar cell presented above. Each subcell is shown with passivation layers and tunnel junction interconnects. It should be noted that for this figure the tunnel diode layers were made thicker to reveal the band bending which shows the majority carrier states separated by a thin barrier. In the case of the top tunnel diode, it is clear that even very thin layers will absorb photons meant for middle junction cell. This could lead to a tradeoff between series resistance and middle junction current. The development of high bandgap tunnel diodes at the lattice constants of interest to this project is a critical research objective to this work, although not a part of this dissertation.
Figure 2.8: Band diagram representation of the full three junction, n+p solar cell device at zero bias showing each of the three subcells with window and BSF layers as shown in Figure 2.6. Two GaAs$_{0.90}$P$_{0.10}$ tunnel junctions connect the three junctions. The GaP/Si nucleation is here shown as the window/emitter interface of the Si subcell with the n-type GaP layer acting as window.

2.2.6 Concentrator Solar Cells

Equation 2.19 also indicates that the effect of series resistance will play a major role in the operation of a solar cell under concentration. Under concentrated light, the current produced by a solar cell increases linearly to first order. The open circuit voltage increases logarithmically, following the relationship between $V_{OC}$ and $J_L$ of $V_{OC} =$
\( \frac{n k T}{q} \ln \left( \frac{j_n}{j_0} + 1 \right) \) \hspace{1cm} \text{Equation 2.4 and shown experimentally in Figure 2.9.} \]

The efficiency increases along with these two parameters until the FF begins to limit performance via the onset of series resistance effects arising from high current density. A series-resistance associated power loss of \( J^2 R_s \) shows that for concentrator solar cells anything affecting series resistance is extremely important. This includes contact resistance, tunnel junction resistance, semiconductor resistance (especially in the top cell), and grid finger resistance. The plots of Figure 2.9, which show FF, efficiency, and \( V_{oc} \) as a function of concentration from the world record efficiency solar cell of Reference [10], demonstrate the common behavior of a solar cell under concentration with a maximum efficiency occurring at some magnitude of concentration before the FF-led degradation. Significant efficiency gains and therefore large increases in power output are afforded by concentrating the light incident on a solar cell. Indeed, it is this practice that enables the terrestrial use of high-efficiency III-V photovoltaics [11-14].
2.3 Conclusions

This chapter has shown how multijunction solar cells are able to attain high efficiency. The basic, common sense notion of converting solar energy more effectively with a MJ has been known for decades. The rise of multijunction solar technology required years of research to open up access to the lattice constant-bandgap map, to improve the quality of the important materials (i.e. minimize \( W_{OC} \)), and make advances on the other components necessary, such as tunnel junctions. The bandgap requirements for the middle and top III-V subcells based on a Si subcell were derived from the ideal, radiative-limit Shockley-Quiesser model. The basic strategy for achieving those bandgaps follows from a GaP/Si nucleation layer to a GaAs\(^{y}P_{1-y}\) metamorphic buffer and GaAs\(_{0.90}P_{0.10}\) and...
Ga$_{0.57}$In$_{0.43}$P junctions. This strategy involves many challenges. Of these challenges, three are particularly relevant to the work of this dissertation. First, the GaP/Si interface is critical because it naturally invites a host of crystalline defects. Metamorphic step-graded buffers which minimize the threading dislocation density are critical for maintaining high PV performance. Finally the creation of a high bandgap top cell is not a trivial undertaking. Ga$_x$In$_{1-x}$P brings its own set of issues, and the while study of its alloy lattice matched to GaAs has been underway for decades, Ga-rich (higher bandgap) compositions have only recently begun to receive research efforts. These three topics are the focus of Chapter 3.

2.4 References


Chapter 3

Epitaxial Challenges

As is mentioned in the introduction, one of the major advantages afforded by III-V semiconductor materials is the freedom to adjust lattice constant and bandgap to suit the aims of the desired device design. The introduction also discusses the overarching purpose of this work: to combine the flexibility and high performance III-V semiconductors, specifically Ga$_x$In$_{1-x}$P, with Si substrates and subcells. The topic of this chapter will be to describe the materials challenges associated with this goal, which can be organized into three main issues. First, in order to realize the flexibility of III-V material bandgaps, the lattice constants must be tunable. Epitaxial growth of crystallographic materials with different lattice constants leads to defects in the crystal structure which must be understood and managed. Second, the growth of high quality III-V materials on Si substrates requires the circumvention of a number of very serious materials mismatches. Third, the epitaxy of Ga$_x$In$_{1-x}$P alloys is known to give rise to two forms of group III lattice segregation which can have significant impacts on materials properties: CuPt$_B$ ordering and phase separation. These issues are discussed in this chapter.
3.1 Lattice Mismatched Epitaxy

Lattice mismatched epitaxy is the growth of an epitaxial layer with a lattice constant different from the lattice constant of the host layer. The difference is known as misfit. Misfit ($f$) is described quantitatively by:

$$f = \frac{a_0 - a_e}{a_0} \quad \text{Equation 3.1}$$

During growth of a mismatched layer, misfit results in the development of a coherent strain in the epitaxial layer where the in-plane crystal lattice will adjust to conform to the substrate lattice while the out-of-plane crystal bonds stretch or compress (depending on the sign of the mismatch) away from the equilibrium lattice spacing in response to the in-plane elastic deformation. The amount of this deformation depends on the elastic properties of the film, i.e., Poisson’s ratio. A compressive (tensile) strain results from an epilayer with a lattice constant larger (smaller) than the substrate. This is shown schematically in Figure 3.1 (a) and (b) where the lattice constant of the epitaxial layer is greater than that of the substrate, resulting in a compressive strain and an elongation of the out-of-plane bonds.
As the layer grows and the thickness increases, the strain increases as well. At some thickness known as the critical thickness ($h_c$), it becomes energetically favorable for some of the bonds in the lattice to break, forming misfit dislocations as shown in Figure 3.1(c). That is, it is no longer energetically favorable for the epilayer to remain coherent with the substrate and the energy required to form a misfit dislocation is equal to the strain energy released by the dislocation. As misfits are formed, the epilayer is allowed to return to its equilibrium lattice constant. The formation of misfits and the change of the epilayer’s crystal lattice constant to its equilibrium value is known as relaxation and defines the growth regime known as metamorphic growth. The extent of this relaxation depends on many factors including the amount of misfit, layer thickness, and growth temperature; a layer may be partially relaxed with a lattice constant somewhere in between that of the substrate and its own equilibrium lattice spacing.
For more information, the measurement and calculation of relaxation and strain behavior in epitaxial layers is covered in Chapter 4, “Experimental Techniques”, where the X-ray diffraction (XRD) technique is described. Additionally, the critical thickness of a layer can be calculated following theories from references [1-3].

### 3.1.1 Dislocations

In the growth of metamorphic III-V materials with zinc-blend crystal lattices, such as GaAs, GaP, InP, and related alloys, the most important misfit dislocations that form to relieve the misfit strain are of the $\frac{1}{2} <110>$, $60^o$ type, named for the $60^o$ angle between their Burgers vector and line direction. Since a dislocation cannot terminate within a crystal (it must reach an edge or surface), every misfit dislocation created has an associated segment that threads to the surface of the film. The threading segments of these glissile dislocations glide on {111} planes.

planes and increase the length of the strain-relieving misfit dislocations which run along the interface. A misfit and threading dislocation and their glide behavior are shown schematically in Figure 3.2. As a dislocation glides through a layer, it may encounter another dislocation of appropriate Burgers vector and annihilate.

The electronic defect states associated with threading dislocations can extend through device junctions and result in shunt current pathways. These states can have a major impact on device performance by, for example, acting as recombination centers in the active layers of a solar cell. Yet they are necessary to achieve relaxed metamorphic layers. The direct growth of III-V materials on Si results in extremely large threading dislocation densities on the order of $10^9$ cm$^{-2}$ or higher. Due to the importance of the ability to adjust the lattice constant of an epitaxial layer away from that of the substrate, a lot of
effort has been directed toward achieving high quality, relaxed metamorphic materials with low TDD.

3.1.2 Strategies for Reducing Threading Dislocation Density

From the discussion above, it follows that one potential method for reducing threading dislocation density (TDD) is to simply grow very thick layers. As the thickness of the epilayer increases, the distance a threading dislocation can glide increases and the increased probability of dislocation interactions reduces the overall dislocation density. Unfortunately, the thickness required to grow highly mismatched epilayers with low dislocation density is unreasonably large and so this is not a solution. For a GaAs film grown on Si (~4% mismatch) with a thickness of about 2 microns, the threading dislocation density can be reduced to $10^7$ or $10^8$ cm$^{-2}$, still far too high for device application [4].

Another potential strategy for TDD reduction is thermal cycling. Since mismatched epitaxial materials generally have different coefficients of thermal expansion, strain can be induced with temperature changes. Strain can then drive dislocation glide while high temperatures reduce the energetic barrier to glide thereby increasing the likelihood of dislocation interactions. Thermal cycling was not found to be sufficient, however, with reductions in threading dislocations resulting in a density of about $10^8$ cm$^{-2}$ [5].
The most successful and widely used method to grow metamorphic materials with low TDD are compositionally-graded metamorphic buffers for which the aim is to change the lattice constant gradually, introducing threading dislocations in a controlled manner before reaching the target lattice constant. Two general strategies have been employed: linear grading and step grading in which the lattice constant is adjusted by changing material composition. Linear grading involves the gradual change in lattice constant over the layer thickness. Step grading (Figure 3.2 (a)) involves creating a series of low mismatched interfaces, changing the material composition at each step. If the misfit for each step is low, the threading dislocation density required to achieve full relaxation can be small.

Properly designed step-graded buffers are theoretically better than linear-graded buffers at reducing TDD for a given lattice constant change. This is due to the presence of a number of low mismatch interfaces which abruptly introduce small amounts of strain.
This strain helps drive the dislocations already nucleated at the first mismatched interface to glide (Figure 3.2(b)) and so strain is relieved more from gliding existing dislocations than by nucleating new dislocations. Care must be taken, however, to introduce enough strain to increase the glide rate (which has a linear relationship with strain) while not increasing the nucleation rate (which has an exponential relationship with strain) [6].

The conclusion of the previous discussion is that high growth temperature and moderate levels of strain constitute the preferred growth strategy for minimizing TDD in a step-graded buffer. In general, the number of misfit dislocations per area can be predicted with the following equations [7]. Strain relief is related to glide velocity by the following equation:

\[
\delta = \frac{p_t b v}{2} \quad \text{Equation 3.2}
\]

Where \( \delta \) is the rate of mismatch strain relief, \( v \) is the dislocation velocity, \( b \) is the magnitude of the Burgers vector, and \( p_t \) is the threading dislocation density. The empirical expression for dislocation velocity is:

\[
v = BY^m \varepsilon_{\text{eff}}^m e^{-u/kT} \quad \text{Equation 3.3}
\]

Where \( B \) is a constant, \( Y \) is the biaxial Young’s modulus, \( \varepsilon_{\text{eff}} \) is the effective strain on the dislocation, \( m \) is a fitting parameter typically between 1 and 1.2, and \( U \) is the activation energy for dislocation glide. Combining Equations 3.2 and 3.3 and solving for dislocation density gives:

\[
p_t = \frac{2R_g R_{\text{eff}} e^{kT} U}{b BY^m \varepsilon_{\text{eff}}^m} \quad \text{Equation 3.4}
\]
From Equation 3.4 it is apparent that growth rate, grading rate, and temperature are the parameters that can be used to minimize the TDD. Unfortunately, all of these have practical limits. The growth rate cannot be reduced to the point where extremely long growth times are required. Likewise the grading rate cannot be reduced to the point where graded buffers are extremely thick, both for practical purposes and for thermal mismatch cracking issues. Temperature turns out to be the most useful of the parameters, but again there are practical issues depending on the growth technique (e.g., gas source nucleation in CVD) and material properties (i.e., decomposition temperatures, vapor pressures, etc). For reasonable values of the parameters in Equation 3.4, it is found that the dislocation density required for full relaxation for step-graded buffers systems is on the order of $10^5$-$10^6$ cm$^{-2}$, depending on material system [7].

One of the primary results of this work, the high temperature growth of GaP via MBE and MOCV (Chapter 5), was motivated by the desire to use high growth temperatures to control threading dislocations. Since GaAs$_y$P$_{1-y}$ is to be used as a metamorphic buffer that can span the lattice constant range from GaP/Si all the way up to compositions of $y = 90\%$, the ability to grow high-quality GaAs$_y$P$_{1-y}$ at high temperatures is critical for the promotion of dislocation glide and TDD minimization.

### 3.2 III-V/Si Planar Material Integration

As mentioned in the introduction of this dissertation, the growth of III-V materials on Si has been an object of interest for decades. Experimental efforts over the last several decades, however, have proven that the integration of the two material systems is not trivial [8-11]. Mismatches in lattice constant, coefficient of thermal expansion, and the nature of polar/nonpolar material interfaces can cause threading dislocations, micro cracks, and anti-
phase domains (APDs), respectively. As mentioned in the introduction, extensive work on heterovalent interfaces has led to APD-free, low dislocation III-V materials on Si. This has been accomplished within our group and through several collaborations via two different strategies. The first was to use high quality SiGe graded buffers [12, 13] coupled with high quality GaAs/Ge nucleation. The key innovations from this work regarding the III-V/IV nucleation were the use of vicinal substrates and the precise control of nucleation [14-19]. The potential for high quality III-V growth on Si was thus achieved as successful solar cells were created via this methodology [20, 21]. These innovations were carried over to become key components of methodology used for GaP/Si and are discussed in more detail below.

Another strategy is to use GaP/Si virtual substrates since GaP is closely lattice matched to Si (0.37% at 300K). For the purpose of this dissertation research, we are only interested in GaP-based nucleation as this is the pathway to achieving a large bandgap graded buffer; note that Si$_x$Ge$_{1-x}$, which spans the same lattice constant range, has a bandgap that is always much lower than the III-V upper junction subcells and is also smaller than the Si substrate upon which it is grown. Thus Si$_x$Ge$_{1-x}$, while very successful as an integrating buffer for III-V/Si in general, is not appropriate for the intended application where the Si substrate also will become a high efficiency lower junction subcell. This is depicted in Figure 2.5 in Chapter 2.

The epitaxial growth of GaP on Si has been of interest for decades as well [8-11, 22-24] but only recently has work on the epitaxial growth of GaP/Si demonstrated high quality, defect-free planar GaP layers on Si [25, 26]. In this section the issues making GaP/Si such a challenging materials problem will be discussed. Some of these factors are
equivalent to those present for the GaAs/Ge system, such as the nature of polar on nonpolar epitaxy. GaP/Si is more challenging, however, due to phosphorous-silicon reactivity, greater difficulties involving the coefficients of thermal expansion, and a greater lattice mismatch.

### 3.2.1 Polar on Nonpolar Epitaxy

Growth of III-V polar compounds on a nonpolar group IV substrates results in the loss of a degree of freedom with respect to crystalline orientation of III-V materials such that the III-V crystal registry may be shifted by one half unit cell, resulting in APDs (Figure 3.3) which are electrically active and potentially detrimental to devices. To combat this issue in the GaP/Si system, a vicinal substrate in conjunction with a high temperature (~950°C) pre-growth anneal is used to induce a double-stepped atomic Si surface [24]. The double stepped surface allows for correct crystal registry of the GaP grown subsequently as shown in Figure 3.3.

![Figure 3.3](image.png)

(a) **Single Atomic Stepped Surface**

(b) **Double Atomic Stepped Surface**

Figure 3.3: Images showing interface between a group IV crystal and a III-V binary crystal with the group IV crystal exhibiting a single stepped surface (a) and a double stepped surface (b).
3.2.2 Elimination of Contamination

Additionally, it is vital that the starting substrate surface be pristine. Surface contaminants must be avoided to minimize defect-causing heterogeneous nucleation sources. An important point here is that threading dislocations, as discussed previously in this chapter, have been described as arising from homogenous misfit dislocations resulting from the lattice mismatch of the epitaxy. Heterogeneous nucleation sources, which can be due to substrate crystal imperfections or surface contaminants, can reduce the activation energy for dislocation nucleation, thereby increasing the total density beyond what is necessary to accommodate the lattice misfit. Carbon and oxygen are especially problematic in this regard as Ga, As and P bond more strongly to them than to Si or Ge, as shown in Table 3.1.

Table 3.1. Minimization of heterogeneous nucleation sources due to contamination in GaP/Si nucleation is accomplished in part by a thorough chemical clean of the Si substrate. While effective, an ex-situ clean was not found to be sufficient for the complete elimination of nucleation-related heterogeneous defects, perhaps because such high annealing temperatures, even in ultra-high vacuum, can introduce contamination species that cannot be removed once under vacuum. In order to bury any residual contamination, a thin (~20 nm) homoepitaxial layer is grown on the substrate surface prior to nucleation.
Table 3.1: Diatomic bond strengths showing that III-V atoms (gallium, arsenic, phosphorous) bond strengths with carbon and oxygen are stronger than those with silicon and germanium.

<table>
<thead>
<tr>
<th>Diatomic Bond Strengths (eV)</th>
<th>Ge</th>
<th>Si</th>
<th>C</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>2.4</td>
<td>2.6</td>
<td>3.5</td>
<td>3.9</td>
</tr>
<tr>
<td>As</td>
<td>3.1</td>
<td>---</td>
<td>4.8</td>
<td>5.0</td>
</tr>
<tr>
<td>P</td>
<td>---</td>
<td>3.8</td>
<td>5.3</td>
<td>6.1</td>
</tr>
</tbody>
</table>

3.2.3 Ga-First Migration Enhanced Epitaxy (MEE)

Despite the relatively small lattice mismatch between GaP and Si, the high energy associated with a polar/nonpolar interface causes island bunching in the first phases of growth, which in turn leads to various crystal registry defects such as microtwins and stacking faults [27]. It was found that these defects could be minimized with the use of a low temperature migration enhanced epitaxy (MEE) process by which the substrate is exposed to carefully controlled doses of Ga and P independently, coercing the film into a 2D growth mode. This nucleation process is well suited to solve another materials issue with GaP/Si growth: phosphorus-silicon reactivity. Phosphorus atoms are known to roughen the Si surface by displacing Si atoms [28] and the initiation of the MEE process with Ga can solve this problem by preventing the Si surface from coming into direct contact with the P dose.
3.2.4 Successful elimination of nucleation-related defects

Figure 3.4 shows cross-sectional transmission electron microscope (XTEM) images of the GaP/Si interfaces of both an unoptimized and a fully optimized GaP/Si nucleation. In image (a), a very rough, highly defective interface is observed while image (b) shows no heterogeneous, nucleation-related defects and only misfit dislocations, which are unavoidable, are visible. In both images, the layer grown is 0.5 µm thick, well above the critical thickness of around 50 nm. Because of this, misfit dislocations are expected.

![Figure 3.4: Cross-sectional transmission electron microscope (XTEM) images showing (a) the defect-riddled, rough interface of an unoptimized GaP/Si nucleation and (b) the heterogeneous-defect-free, smooth interface of a fully optimized GaP/Si nucleation process.](image-url)
3.2.5 Successful elimination of nucleation related-defects by MOCVD

GaP/Si (100) layers that are simultaneously devoid of SFs, MTs, and APDs were also grown by MOCVD [26]. The approach generally followed that for the MBE-based methodology. The misorientation of the Si substrates, Si epitaxy prior to GaP nucleation, and the use of Ga-initiated layer-by-layer nucleation process were central to growth in the MOCVD system as well.

3.3 Ga\textsubscript{x}In\textsubscript{1-x}P epitaxy

As stated earlier, another major goal of this research is to investigate the epitaxy of Ga\textsubscript{x}In\textsubscript{1-x}P layers and the formation of photovoltaic devices at relatively unexplored Ga-rich compositions in order to access an appropriately large bandgap for the top sub-cell. Therefore, a review of the history of the growth and material properties of Ga\textsubscript{x}In\textsubscript{1-x}P is essential and is given in this section.

Studies regarding the epitaxy of Ga\textsubscript{x}In\textsubscript{1-x}P have revealed two important microstructure-related defects. The first is a segregation of indium and gallium atoms to alternating \{111\} planes, known as CuPt ordering (Figure 3.5). The second, which is referenced under several different names in the literature, most commonly phase separation or composition modulation, is the larger scale separation of the alloy into Ga-rich and In-rich regions. Both of these are worth a detailed understanding and will be discussed in this section. Most of the following discussion reflects the fact that the majority of research regarding Ga\textsubscript{x}In\textsubscript{1-x}P has focused on the composition lattice matched to GaAs (x ~ 0.51). Section 3.3.4 expands the discussion both to the Ga-rich compositions of interest in this dissertation as well as to the impact of these features on solar cell devices.
3.3.1 CuPt\textsubscript{B} Ordering: History and Mechanism of Formation

Early studies involving MOCVD-grown Ga\textsubscript{0.51}In\textsubscript{0.49}P lattice matched to GaAs revealed that different growth conditions resulted in different values of the measured optical band gap. First reports (see ref. [29] and cited works therein) referred to this as the “50 meV” problem for which different studies reported measurements of room-temperature band gap varying from 1.85 to 1.90 eV, posing an important uncertainty (~ 200 Å photon wavelength) to researchers motivated by the fabrication of AlGaInP-based visible lasers. The effect was known to be sensitive to growth conditions; the optical band gap decreased when the growth temperature was lowered from 700°C to 650°C but the mechanism was
not initially understood until preliminary evidence for the connection with atomic-scale arrangement was presented in 1986 [29].

Confirmation of the relationship between the bandgap reduction and the ordering of group III atoms was provided by PL, Raman scattering spectroscopy and TEM [30, 31], and also by polarized PL measurements [32]. The presence of CuPt ordering is most often confirmed by the presence of extra reflections in the transmission electron diffraction (TED) patterns at one half the distance to the 111 zinc-blend reflections [30]. In this way it has also been confirmed as type “B” CuPt ordering in which the self-organization is found in the {111} and {111} planes (CuPtA would be the other two {111} planes). The effect of CuPtB ordering is to double the crystal unit cell, halving the Brillouin zone. The conduction band state at the L point is then zone folded back onto the T point. These like-symmetry states repel one another resulting in the reduction of the bandgap [33, 34].

It was shown by detailed thermodynamic studies that a CuPtB ordering is not energetically preferred for a Ga0.51In0.49P crystal [35]. The cause was therefore expected to be related to the surface structure during growth. Philips et al. [36] proposed a non-random group III incorporation mechanism caused by the formation of phosphorous dimers on the growth surface. Other theoretical calculations [37] and experiments [38] agreed and showed that CuPtB type ordering is energetically favorable under (2×1) surface reconstructions. Surface dimerization causes compressed and dilated atomic sites in the first few subsurface layers, causing the segregation of group III atoms due to the fact that In has a much larger covalent radius than Ga. CuPtB ordering is therefore an energetically favorable surface structure that is frozen into the bulk crystal during growth. For less P-rich surface reconstruction, such as a (2×4), CuPtB ordering is not expected [38].
The degree of ordering can vary between completely disordered, where the distribution of group III atoms is completely random, to completely ordered, where Ga and In atoms are completely separated to alternating \{111\} planes. It is useful to define an ordering parameter as $\eta = 0$ for completely disordered and $\eta = 1$ for completely ordered. In general, the ordering parameter is found to be in the range of 0.3 to 0.6 for most conditions of film growth [39]. The ordering parameter is generally estimated by bandgap measurements as compared with the completely disordered bandgap of 1.910 eV [40], but can also be measured by XRD [41].

3.3.2 CuPt8 Ordering: Dependence on Growth Conditions

Concurrent with efforts to understand the ordering mechanism and its effects on the material, work was undertaken toward connecting the degree of ordering and the associated bandgap change with growth conditions. In order for high quality devices to be fabricated, this aspect of the alloy must be understood and controlled in order to achieve target bandgaps, especially when one considers the control of ordering as a tool for adjusting bandgap while maintaining a given composition. This has been used in solar cells where the emitter and base layers have been grown to be slightly ordered and the back-surface field disordered to achieve minority carrier blocking at the base-BSF interface.

In the MOCVD growth environment, the presence of ordering has been shown to depend on all major growth parameters. Ordering is maximized for undoped Ga$_{0.51}$In$_{0.49}$P and has been shown to decrease and disappear entirely for various doping types and concentrations [42-44]. The relationship between ordering and the V/III ratio has been shown to be subordinate to growth temperature [30]. Substrate orientation was also found
to affect ordering [38], but as with V/III ratio, the relationship between ordering parameter and substrate offcut appears to depend on the growth temperature.

The magnitude of group III ordering in Ga$_{0.51}$In$_{0.49}$P and the growth temperature and growth rate were found to have a complicated relationship useful for the conceptual understanding of CuPt$_B$ ordering. A model proposed by Kurtz et al. [45] considers several cation adatom time scales. The first, $t_s$, is the surface residency time, from arrival on the surface to incorporation in the crystal, equivalent to $L_s/R_g$, where $L_s$ is equal to the thickness of one monolayer and $R_g$ is the growth rate. The second is $\tau_s$, the time required for Ga and In atoms to relax into the ordered state. To first order, $\tau_s$ is given by $\delta_s^2/D_s$, where $\delta_s$ is a length on the order of several atomic spacings and $D_s$ is the surface diffusion constant for Ga and In adatoms. An ordered surface occurs when the residence time ($t_s$) on the surface is greater than the time it takes an adatom to diffuse and find its preferred (ordered) position ($\tau_s$). It follows then that for decreased growth temperature (smaller diffusivity and therefore shorter $\tau_s$) or for increased growth rate (shorter $t_s$), the degree of ordering should decrease. These are indeed two of the trends observed experimentally [45].

This dependence was complicated as the degree of ordering (as interpreted from bandgap measurements) was found to peak at intermediate growth rates and temperatures and fall again as either parameter increased. To explain this, the subsurface layer, the transition layer between the bulk and the surface during growth, must be taken into account in the previous model. In the subsurface layer the group III diffusion coefficient is still large enough for significant reorganization but the disordered state is a lower, preferred energy configuration than the ordered (as in the bulk crystal and contrary to the surface where the surface reconstruction dictates the preferred configuration). Consider then two
more time scale parameters: $t_r$, the residence time in the transition layer, equal to $L_t/R_g$ where $L_t$ is the transition layer thickness, and $\tau$, the time it takes for randomization in the transition layer. As growth temperature is increased (greater subsurface diffusivity and therefore shorter $\tau$) or growth rate is decreased (greater residency time in the subsurface region $t_r$), ordering will also decrease. This explains the trends found in reference [45] by describing competing processes on the crystal surface and in the subsurface layer.

This simple model explains well the convoluted relationship between growth rate, temperature and degree of ordering in Ga$_{0.51}$In$_{0.49}$P. Current strategies for controlling order involve using high growth temperature and large V/III ratios [39, 46]. Use of antimony as a surfactant to alter the surface reconstruction during growth is also effective but care must be taken to avoid incorporation for device-quality growth [46-48].

3.3.3 CuPt$_B$ Ordering: Molecular Beam Epitaxy (MBE)

The previous discussion focused on MOCVD-based growth of Ga$_{0.51}$In$_{0.49}$P, on which the majority of published literature studies are based. The MOCVD growth environment affords a far greater degree of freedom for the growth of Ga$_x$In$_{1-x}$P than MBE because of limitations imposed by In desorption in the MBE environment such that growth temperatures are limited to about 500°C [49, 50]. Because of this limitation, it seems that the MBE environment cannot provide a great amount of control over CuPt ordering. Articles that comment on CuPt$_B$ ordering in Ga$_x$In$_{1-x}$P have found either no evidence of ordering [51, 52], or a weakly ordered alloy [53, 54]. Other kinds of unintentional microstructure, phase separation or composition modulation (CM), were reported, however [51, 55, 56].
3.3.4 Composition Modulation

Composition modulations are widely observed in III-V alloys and are described as coherent regions of different composition which result in lattice strains that can be observed as contrast in TEM images [57]. While receiving far less attention than CuPt$_B$ ordering, several types of this composition modulation for Ga$_x$In$_{1-x}$P have been reported, including variations perpendicular to the growth surface known as fine scale (~10 nm) and large scale (>~ 100 nm) as well as modulation parallel to the growth surface. Figure 3.6 shows various examples of XTEM images from the literature of composition modulations in Ga$_x$In$_{1-x}$P. As an initial guess, it would be reasonable to imagine composition modulation resulting from spinodal decomposition, a well-known phenomenon in which alloys within their miscibility gap create compositional fluctuations to lower their free energy without forming precipitates. Common growth temperatures, however, are not high enough to destabilize Ga$_x$In$_{1-x}$P films sufficiently to cause significant bulk diffusion [58]. Most calculations put the Ga$_{0.5}$In$_{0.49}$P miscibility gap well below common growth temperatures, even for MBE [39]. Like CuPt$_B$ ordering, it is believed to be the result of a surface driven mechanism. Bulk diffusion is not even sufficient to allow post-growth annealing to randomize the composition modulated regions [46].
Figure 3.6: XTEM images of composition modulation in Ga\textsubscript{x}In\textsubscript{1-x}P from the literature. (a) Ga\textsubscript{0.77}In\textsubscript{0.23}P grown by MOCVD on GaAs\textsubscript{y}P\textsubscript{1-y}/GaP graded buffer [46]. (b) Ga\textsubscript{x}In\textsubscript{1-x}P grown by MBE slightly lattice mismatched from GaAs with strain = 0.39\% [51]. (c) CM in GaP/InP short-period superlattices grown by MBE [59]. Ga0.52In0.48P grown lattice matched to GaAs by MOCVD [39].

Composition modulations in III-V semiconductors have been exploited to achieve quantum structures in short period superlattices [58]. As such, many characteristics of compositional modulation have been discovered through superlattice studies. It has been shown that strain resulting from lattice mismatch between super lattice layers drives composition modulation [60]. It has also been found to be anisotropic based on the fast and slow diffusion directions on the growth surface, adding evidence to the conclusion that it
is a surface driven phenomenon [58, 60]. Composition modulation is also believed to be
driven by surface undulations which are a natural result of strained layers. At the crests of
surface undulations in a crystal the lattice is dilated, at the troughs it is compressed. This
influences the bonding sites of the different sized group III atoms [58]. This is especially
important in metamorphic materials for which a “crosshatch” morphology is a standard
characteristic resulting from the strain field of metamorphic layers [61]. This means that
Ga$_x$In$_{1-x}$P may be more prone to composition modulations when grown on metamorphic
substrates with crosshatch even if the layer is not strained, since layers far from
metamorphic buffers nonetheless adopt the crosshatch surface morphology [46]. Other
studies on Ga$_x$In$_{1-x}$P layers, by both MBE and MOCVD, have related the amount of strain
present in a layer to the CM [51, 62]. So either layer strain or surface roughness, or both,
it seems that any process that promotes surface segregation of group III atoms induces CM
with the resultant growth attempting to reduce its free energy by mimicking the structure
and lattice constant of the layer beneath.

Though not nearly to the same extent as CuPt$_B$ ordering in Ga$_x$In$_{1-x}$P, there have
been efforts undertaken to understand how to use growth conditions to control the presence
of CM. A similar conceptual treatment of surface and subsurface as described above for
CuPt$_B$ ordering can be used for CM as well. Just like CuPt$_B$ ordering, phase separation
appears to be a surface driven phenomenon that is not energetically favorable in the bulk.
Unlike for ordering, high growth temperatures are believed to sufficiently increase the
diffusivity in the subsurface layer [45], high growth temperatures did not appear to be
sufficient to randomize composition modulation as diffusion in the subsurface layer is
probably not sufficient to overcome the increased diffusivity on the surface. Mori et al.
found that with very large V/III ratios, CM related defects were eliminated, indicating that by decreasing surface diffusivity, composition modulation can be suppressed [46].

Of course, MBE grown films are limited in growth temperature, so it is not possible to increase the temperature or V/III beyond a certain point to try to reduce defects meaning that MBE-grown films may be victims of the substrate below (i.e., if there is crosshatch or surface roughness). Of course, it is clear that keeping strain to a minimum is vital.

### 3.3.5 CuPtB Ordering and CM with Respect to Ga-rich GaₓIn₁₋ₓP Solar Cells

The most significant effect of CuPtB ordering on the material properties of GaₓIn₁₋ₓP is the bandgap reduction. This has led to the use of disordered material as a back surface field (BSF) for weakly ordered Ga₀.₅₁In₀.₄₉P solar cells [63] with very small interface recombination velocities [64]. The presence of ordering does not have a major impact on material quality or device quality. While studies have suggested increased minority carrier lifetimes for the ordered alloy [65-67], these studies were performed either on not-intentionally-doped (nid) samples, or at low temperatures, and so it is difficult to relate to actual solar cell devices.

As stated, work on GaₓIn₁₋ₓP regarding CuPtB ordering has been largely confined to the lattice matched case until recently. Mori and Fitzgerald [46] found that high growth temperatures in the MOCVD environment resulted in disordered Ga-rich (x = 0.6 – 0.8) GaₓIn₁₋ₓP. Steiner et al. [68] related the ordering parameter (as controlled by a surfactant, Sb) to bandgap for a variety of MOCVD-grown, Ga-rich compositions from x=0.51 to x = 0.76, as shown in Figure 3.7. From this set of data, which shows theoretical curves of the material bandgap vs. composition for ordering parameter, η, of 0, ½, and 1, as well as experimental data points at many different compositions, one can estimate the degree of
ordering in a sample based on the measured bandgap and measured alloy composition. Few reports on Ga-rich compositions of Ga$_x$In$_{1-x}$P grown by MBE are available, but samples grown by Simon et al. showed no indications of CuPt$_B$ ordering [52].

![Figure 3.7](image)

Figure 3.7: Theoretical curves (lines) and experimental data (circles) of measured bandgap for different compositions of Ga-rich Ga$_x$In$_{1-x}$P for different values of ordering parameter from ref. [68]. Curves corresponding to $\eta = 0$, $\eta = 0.5$, and $\eta = 1$ are plotted.

The precise effects of CM on material quality and device performance are still unclear, especially as it can exist concurrently with CuPt$_B$ ordering [39] and, like CuPt$_B$
ordering, can reduce bandgap and change emission properties [69, 70]. Composition modulation in Ga-rich compositions of metamorphic Ga$_x$In$_{1-x}$P is known to be extremely harmful to optical quality [46]. In other reports, it has been observed to have little or no effect on optical quality for the composition lattice-matched to GaAs [39]. These seem to be contradictory findings, but it must be kept in mind that, as discussed previously, CM is not only sensitive to strain and surface morphology, but also interacts with threading dislocations [71, 72]. These facts indicate that CM may be relatively benign for lattice matched cases, or for small magnitudes of modulation, but where strain is present, surface morphology is non-planar and threading dislocations are present, it may be significantly detrimental. More studies are probably required, however, to relate presence of CM to actual device metrics. Nonetheless, one extremely important consequence of the strain dependent behavior of CM is that it is especially problematic as a material for step graded buffers. Since Ga$_x$In$_{1-x}$P spans such a wide range of both lattice constant and band gap, it presents an attractive ternary material for metamorphic grading. Growth of Ga$_x$In$_{1-x}$P step-graded buffers led to very high TDD due to CM related defects blocking the glide of dislocations [71]. This is, in fact, the primary reason why GaAs$_y$P$_{1-y}$ graded buffer layers are preferred in this work to Ga$_x$In$_{1-x}$P, which spans the same lattice constant range of interest but does not show significant phase separation issues.

### 3.4 References


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Chapter 4

Experimental Techniques

4.1 Growth Techniques

4.1.1 Molecular Beam Epitaxy (MBE)

Solid source molecular beam epitaxy (SSMBE) is a common growth technique capable of extremely high levels of purity and precision. The technology which facilitates growth by the MBE system has been covered in many references [1-4]. A modified Varian Gen II SSMBE system was used for all of the MBE growth in this dissertation. Crystal growth in SSMBE is controlled by the precise regulation the substrate temperature and of the molecular beam fluxes. Very high purity source materials together with ultra-high vacuum (UHV) conditions, i.e., \( \leq 10^{-10} \) Torr, allow very high levels of control of molecular beam fluxes and deposition conditions resulting in monolayer-precision growth. The UHV environment ensures long mean free paths of species to allow for highly directional molecular beams.
Figure 4.1: Schematic of a Molecular Beam Epitaxy System [4].

Figure 4.1 shows the basic setup of an MBE system with effusion cells, shutters and some basic vacuum system components shown. Vacuum is maintained by a combination of different types of pumps and a cooling shroud. A substrate manipulator is present to enable molecular beam flux measurements to be made by a special ion gauge in the exact same physical location as growth. Substrate temperatures are measured both by a thermocouple positioned in close proximity to the substrate heater and by an infrared pyrometer position outside the system with a line of sight through a viewport normal to the sample surface. The infrared pyrometry allows a direct and highly accurate (given an accurate calibration) measure of sample temperature by detecting thermal radiation.
emanating from the sample surface. The pyrometer is calibrated to the GaAs native oxide desorption temperature.

Also included in MBE systems is a Reflection High Energy Electron Diffraction system, which will be described shortly. Molecular beam fluxes are controlled by the temperature of effusion cells, which house the group III sources (Ga, In, and Al) and the dopant sources (Si and Be) and are heated by resistive elements.

For group V elements, As and P, valved cracker sources are used. A schematic of the P source is shown in Figure 4.2 in which three “zones” are shown, the red zone, the white zone and the cracking zone. Phosphorous is loaded as red phosphorous into the red zone where it is converted into white phosphorous and stored in the white zone by a process in which the red zone temperature is increased to 350 - 400°C inducing sublimation of the red phosphorous. The white zone is cooled to a temperature of ~50°C, thereby collecting the sublimated material. White phosphorous is desired for its higher vapor pressure, which allows for a more stable flux of P molecules. The reason white phosphorous can’t be loaded directly is that it has the extremely dangerous characteristic that it ignites in the presence of oxygen. Under standard growth conditions, the white zone is maintained at ~70°C to provide an appropriate flux for growth. At this temperature the flux is composed of P₄ molecules. After passing through a high temperature cracking zone (800 - 950°C), a portion of the P₄ flux is converted into P₂ dimers, which have a simpler incorporation mechanism and generally provide higher quality material. There is a tradeoff, however, between raising the cracker temperature to get a more pure P₂ flux and increased oxygen incorporation that can result from these high temperatures [5-7].
In general, a species impingent on a crystalline substrate in the MBE environment may undergo a number of processes: adsorption to the surface, migration along the surface, incorporation into the crystal, and thermal desorption from the surface. Group III atoms, for most growth temperatures, have approximately unity sticking coefficient so that the growth rate is determined by group III flux. Group V atoms are much more volatile and do not stick to a substrate in the absence of unbonded group III atoms. This fact is significant because it means that crystals with correct stoichiometry are produced for a range of group V fluxes. Group V flux, along with substrate temperature and growth rate (group III flux),
is therefore one of the controllable parameters that needs to be optimized for growth of high quality material by MBE.

Several growth modes are generally observed in III-V epitaxy by MBE and are depicted in Figure 4.3: (a) island growth (Volmer-Weber; V-W), (b) layer-by-layer (Frank-Van der Merwe), and (c) Stransky-Krastinov (S-K). The growth mode is determined by relative rates of adatom introduction to the surface and removal of adatoms by diffusion and thermal desorption. Volmer-Weber growth involves the nucleation and propagation of three-dimensional islands and is typically observed for epitaxy of highly strained layers (i.e., high levels of lattice misfit) and results in increased roughness and inhibits accurate control of layer thicknesses and crystalline defects. In the layer-by-layer growth mode, adatoms preferentially bond to surface sites and growth proceeds by the filling in of the surface layer, resulting in very smooth, two-dimensional growth behavior. This is generally the preferred growth mode for coherent epitaxial layers [4, 9]. S-K growth represents a mode somewhere in between V-W and layer-by-layer, where layers are filled in, but some island coalescence does happen, as in Figure 4.3(c).

A fourth growth mode, not shown in Figure 4.3, is known as step-flow growth and is characterized by adsorbed adatoms desorbing or diffusing along terraces and attaching only at step edges. This causes the steps to move along the surface, causing crystal growth without the nucleation of any islands.
Group V sources generally use valved sources in conjunction with a shutter, rather than open effusion cells with shutters, as for Group III sources. This is due to the higher vapor pressure of group Vs. A major advantage to the valved cell is that flux changes can be made instantaneously since a change in source temperature is not needed.

As shown in Figure 4.1, a RHEED system is included in the MBE setup. RHEED is a highly surface sensitive electron diffraction technique where an electron beam is directed at a glancing angle toward the substrate before, during, and after growth. Opposite the RHEED electron gun is a phosphor screen that displays the pattern resultant from the electron beam’s interaction with the semiconductor surface. This pattern can be interpreted in real time to obtain information regarding the surface structure of the sample during
growth. It is an indispensable tool for an in-situ, qualitative check on the progress of a
growth.

4.1.2 Growth: MOCVD

Unlike MBE, which uses elemental sources, MOCVD uses alkalis of group III
elements and hydrides of group V sources. Hydride (H₂) carrier gases are used to bring the
source molecules, in gas phase, to the substrate surface, a vapor-solid interface, where they
are thermally dissociated, leaving the growth elements available to adsorb to the substrate
and incorporate into the crystal. Despite a number of different complicated gas-phase
interactions, a general idea of the growth can still be taken as in MBE [4], in which
adsorption, incorporation, and desorption occur at the growth interface. The growth rate
can be limited by different mechanisms from MBE, however. Since the dissociation of gas-
phase source molecules is temperature dependent, growth at low temperature is highly
temperature dependent and is known as the kinetically-limited regime. As temperature
increases and source decomposition becomes fast, growth rate is limited by the flow of the
sources to the growth surface; this is known as the transport-limited regime. It is in the
transport-limited regime that MOCVD growth is generally performed.

MOCVD growths reported in this dissertation were completed in an Aixtron close-
coupled showerhead MOCVD reactor which can accommodate wafers up to 4” in diameter.
This system uses trimethylindium (TMI\textsubscript{n}), trimethylgallium (TMGa), arsine (AsH\textsubscript{3}),
phosphine (PH\textsubscript{3}), and silane (SiH\textsubscript{4}) and dimethyl zinc (DMZn). For MOCVD growth, the
flow rates of these precursor gases and the substrate temperature are the controllable
parameters for growth. More information on the technology and science of MOCVD
epitaxial methods can be found in References [4, 10, 11].
4.1.3 Comparisons

There are many differences between the MOCVD and MBE growth systems, and so it follows that there are advantages and disadvantages for each. Both techniques have played integral roles in the development of the modern semiconductor industry. While MOCVD tends to allow higher growth rates and higher growth temperatures (often beneficial for material quality), MBE provides faster switching speeds between layers for superior interfaces and in-situ monitoring of surface structures via RHEED. While MBE doesn’t require the use of high toxicity precursor gases, it does require longer maintenance times due to the nature of the UHV environment and significant required baking times to ensure a clean chamber. The decision to use one system over the other comes down to application-specific considerations as both systems are capable of producing extremely high quality semiconductors (both have recently been responsible for world record efficiency solar cells [12, 13]) and economic considerations are too site- and use-specific to allow for a general preference.

4.2 Material Characterization

4.2.1 High Resolution X-Ray Diffraction (HRXRD)

HRXRD measurements are commonly used to measure epi-layer composition, lattice constant, and strain state, all of which are critical to the study of lattice mismatched materials. The fundamental principle of HRXRD is diffraction based on Bragg’s Law, which relates the lattice spacing of the crystalline specimen to the wavelength and angle of incidence of the incident beam of x-rays. Therefore the lattice spacings of an unknown layer can be determined by finding the diffraction angles given a known x-ray wavelength.
The HRXRD system is set up as in Figure 4.4, where the controllable angles of interest are \( V, 2\theta, \chi, \) and \( \phi \). The x-ray source is generally fixed and so the sample and detector are moved for the measurement. For experiments done at OSU, a copper K\( \alpha_1 \) source is used which, with filtering optics, provides an approximately monochromatic radiation, allowing for very high resolution.

Figure 4.4: Schematic diagram of the XRD geometry showing the incident x-rays, sample and detector and the angles of interest.

The single-crystal substrate used for growth has a known lattice constant and is used as a reference. Thus the inter-planar spacings of the epitaxial layer can be determined by finding the Bragg diffraction of the epi-layer and relating it to the substrate. A symmetric diffraction measurement, in which the incident x-ray beam and the detector are at equal angles \( (\omega = \theta) \), can obtain information on the lattice parameter perpendicular to the surface.
of the sample. As explained in Chapter 3, a perfectly relaxed layer will be cubic and have its perpendicular, out-of-plane lattice parameter equal to the in-plane lattice parameters. Often metamorphic layers are not perfectly relaxed and have a tetragonal distortion, meaning that the out-of-plane lattice constant stretches or shrinks to accommodate the strain energy (as discussed in Ch. 3). Performing both symmetric and asymmetric measurements of the sample allows for the determination of both the in-plane and out-of-plane lattice constants which in turn provides for accurate calculation of the relaxation and strain of epitaxial layers. Structure factor considerations for the (001) zinc-blend III-V substrates of interest in this thesis dictate that diffractions from the 004 and 224 planes are used for the symmetric and asymmetric measurements, respectively.

Data from the symmetric and asymmetric diffraction measurements are usually gathered as reciprocal space maps (RSMs). An RSM is created by performing ω-2θ scans at different range of angles of ω away from the substrate diffraction angle. From these RSMs, information is readily gained about the angular separation between the substrate and epi-layer peaks. An example of an RSM is shown in Figure 4.5 where the results from an HRXRD scan of a GaAs$_y$P$_{1-y}$ step-graded buffer are plotted in reciprocal space.
Figure 4.5: Example reciprocal space map (RSM) showing a GaAs$_y$P$_{1-y}$ step-graded buffer grown on a GaP substrate.

The RSM peaks are fitted with Bede Peaksplit software to determine the diffraction angles of each layer of interest. Together with the known miller indices of the crystallographic planes observed, the in-plane (a//) and out-of-plane (a.) lattice constants
can be determined. From these, the epi-layer strain, misfit, and relaxation percentage can easily be calculated:

\[
\text{strain} = \frac{a_s - a_r}{a_r} \quad \text{Equation 4.1}
\]

\[
\text{misfit} = \frac{a_s - a_r}{a_r} \quad \text{Equation 4.2}
\]

\[
\text{relaxation} \% = \left[ 1 - \frac{|\text{strain}|}{|\text{misfit}|} \right] \times 100 \quad \text{Equation 4.3}
\]

4.2.2 Atomic Force Microscopy (AFM)

In this dissertation, AFM is used to measure the surface morphology of semiconductor samples. Measurements of surface morphology can provide a qualitative measure of growth quality as well as evidence for the growth mode. In AFM, a cantilever controlled by extremely precise piezoelectric motors is used to “feel” the surface of the sample and information is transmitted by small deflections in a laser beam reflected off the cantilever and measured by a photodiode, as shown in Figure 4.6. Several different modes are possible for the action of the tip on the surface. In the AFM work presented in this thesis, tapping mode is used. In tapping mode, the cantilever is driven to oscillate near its resonance frequency at amplitudes often much larger than features of the sample surface. The measurement is therefore a measure of the force felt by the cantilever each time it comes into contact with the sample. To detect these forces a laser is directed at the back of the cantilever and the reflection is measured by a photodiode whose signal is processed into an image as the cantilever scans across the sample surface. For the AFM data taken in this thesis, the WSxM software was used for image processing [14].
Figure 4.6: Schematic diagram of AFM system showing a cantilever in contact with the surface of a sample and the laser-photodiode combination to measure deflection in the cantilever.

### 4.2.3 Photoluminescence

Photoluminescence is a technique that directly probes electronic states in a semiconductor sample. Light from a high energy laser is directed onto the sample surface. Photoexcitation of carriers occurs, producing free carriers with energy greater than the bandgap, which then undergo relaxation mechanisms toward the bandgap minimum. The carriers may then recombine radiatively, emitting radiation from the semiconductor which
is collected and measured by a photodetector via a monochromator so that the signal from the sample is measured at discrete wavelengths. The signal from the photodetector is read by a lock-in amplifier coupled to a chopper that acts on the incident laser light.

PL can act as a material quality check in several ways. First, the spectra can be analyzed to determine the bandgap of the material, which can be used to help determine the composition of an alloy. Additionally, spectral peaks associate with impurity and defect levels can be observed. Also, the intensity of the luminescence depends on the amount of radiative recombination, which can be affected by non-radiative recombination mechanisms that are often associated with impurities and defects. Many things can affect the emission spectra from a sample in PL. Defects and impurities (intentional and unintentional), for example, can introduce states within the bandgap of a sample. These can cause carrier recombination that is either radiative or non-radiative. Therefore, direct comparison of PL spectra taken from similar samples with precisely controlled differences can be a powerful diagnostic method.

4.2.4 Electron Beam Induced Current (EBIC) Imaging

EBIC is measured using a scanning electron microscope (SEM). In SEM imaging, the electron emission from a sample surface is measured while being probed by a focused electron beam. The beam scans the sample surface and the resulting secondary electrons are collected and the signal is processed into an image. In EBIC, a p-n or Schottky diode is used. The electron beam is used to generate electron-hole pairs which are then swept through the junction and collected. As the beam is scanned across the sample, the generated current is monitored and used as the imaging signal. Areas of the sample with good carrier collection are bright. Areas containing defects which cause recombination of electron-hole
pairs show up as dark spots. Therefore EBIC is a convenient tool to count threading dislocations given a p-n junction (solar cell) structure. Examples of EBIC images taken from Ga0.57In0.43P subcells on top of various step-graded buffers are shown in Chapter 6.

4.3 Solar Cell Device Characterization

4.3.1 Current-Voltage (I-V)

Both dark and lighted current-voltage measurements are used in this work for PV characterization. Dark current-voltage (DIV) measurements are useful to compare the reverse saturation currents and ideality factors of solar cells, which can give strong indications of the recombination effects in a solar diode junction, as discussed in section 2.2.3, especially when making direct comparisons between similar structures. DIV measurements were performed either with a Keithley 2400 (for quicker analysis) or with a Keithley 6514 electrometer (for detailed analysis with a much lower noise floor) in combination with a voltage source. The collected data are analyzed using Equation 4.4:

\[
J = \frac{V + JR_S}{R_P} + J_{01} \left( e^{\frac{q(V + JR_S)}{n_1 k_B T}} - 1 \right) + J_{02} \left( e^{\frac{q(V + JR_S)}{n_2 k_B T}} - 1 \right) \text{ Equation 4.4}
\]

Where \( R_S \) is the series resistance of the cell, \( R_P \) is the shunt resistance, \( n_1 \) and \( n_2 \) are ideality factors for the two exponential terms, and \( J_{01} \) and \( J_{02} \) are the reverse saturation currents for the two exponential terms. In this equation for the forward bias of a pn junction, derived by Sah, Noyce, Shockley [15], the first term represents the contribution from a parallel shunt resistance, the first exponential describes the diffusion current, with \( n_1 = 1 \), and the second exponential describes the recombination current with \( n_2 \approx 2 \) for a simple
case with a single midlevel trap. The behavior can deviate from that described by \( n_2 = 2 \) in real devices for a variety of reasons, including for an asymmetrical junction \[16\] and for shallow traps contributing to the recombination current \[15, 17\]. The second ideality factor, \( n_2 \), is therefore allowed to vary in the fitting. The fitting is facilitated by the software of Ref \[18\].

Lighted current-voltage (LIV) measurements allow for the direct measurement of solar cell efficiency and provide the parameters introduced in Chapter 2: \( V_{OC}, J_{SC}, \) and FF. LIV curves are measured using a Keithley 2400 source-measurement unit at room temperature. Illumination for LIV measurements was provided by an OAI TriSOL class AAA solar simulator filtered for AM1.5G. Because no reference cell of appropriate bandgap for the large bandgap solar cells of interest in this thesis was available at the time of this work, light intensity was calibrated to yield the EQE-integrated one-sun \( J_{SC} \) of one of the solar cell samples to maintain identical conditions for useful comparison between the different samples.

### 4.3.2 Quantum Efficiency

External quantum efficiency measures a solar cell’s ability to turn incident photons into collected elections. Given a known incident photon flux at a given wavelength \( (\Phi_{inc}(\lambda)) \), a short circuit current measurement provides the number of collected electrons. If all the photons at a given wavelength are absorbed and the corresponding electrons collected by the junction, then the EQE at that wavelength is 100%. Due to the dependence of absorption coefficient on photon energy, EQE is an extremely useful diagnostic tool allowing the response of specific regions of a solar cell to be analyzed. Integration of the response gives an estimate for the total short circuit current of the cell:
The EQE setup used in this work involves a tunable light source from a quartz-halogen lamp connected to a monochromator. A filter wheel is used in front of the monochromator to cut out high order light and ensure monochromatic wavelengths of light. The light is focused and chopped before reaching the sample and the electrical signal from the solar cell is then fed to a lock-in amplifier. Prior to measurement of the solar cell, photodetectors are used to measure the incoming light intensity at each wavelength. Light reflected from the solar cell is also measured using a fiber optic cable connected to a photodetector and this signal is normalized to the reflectance from a mirror of known reflectivity. By measuring the reflectance of a solar cell, internal quantum efficiency (IQE) can be estimated. True IQE must also account for transmission, however, which is difficult to measure for the samples used in this thesis due to the fact that the high bandgap structures are generally grown on materials of lower bandgap.

4.4 Electrical Characterization

4.4.1 Hall Effect

The Hall effect describes the voltage resultant in a conductor transverse to a current and a magnetic field. As in Figure 4.7, where a semiconductor sample with length L, width W and thickness t is shown, an electron flowing through the semiconductor will be deflected by a magnetic field perpendicular to the current flow. The Hall voltage (VH) can be derived as:

\[ V_H = \frac{i \times B}{qtn} \]  

Equation 4.6
Where I is the current passed through the sample, B is the magnetic field, q is the electronic charge and n is the electron concentration in the sample. The Hall coefficient is defined as:

\[
R_H = \frac{E_y}{I_x B} = \frac{V_{Ht}}{IB} = -\frac{1}{nq}
\]

Equation 4.7

From the Hall measurement, given a layer of known thickness and the ability to make low resistance contacts, the carrier concentration can readily be determined.

Temperature-dependent Hall effect measurements are performed on single epitaxial test layers in order to measure the mobility and carrier concentration as a function of temperature. The measurement provides an understanding of the scattering mechanisms affecting carriers as well as the characteristic activation energy of the dopant species used.
The following equation, derived from the charge neutrality equation, describes the concentration of free electrons in the conduction band at a given temperature [20]:

\[
\frac{n_0(n_0 + N_d)}{N_d - N_a - n_0} = \frac{N_C}{g} \exp\left(-\frac{E_d}{kT}\right)
\]

Equation 4.8

Where, for the case of an n-type sample, \(n_0\) is the free carrier concentration, \(N_d\) is the donor concentration, \(N_a\) is the compensating acceptor concentration, \(k\) is the Boltzmann constant, \(g\) is the degeneracy factor, \(E_d\) is the ionization energy of the donor level and \(N_C\) is the effective density of states given as

\[
N_C = 2 \left(\frac{2\pi m^* kT}{\hbar^2}\right)^{3/2}
\]

Equation 4.9

Where \(h\) is the Planck constant, and \(m^*\) is the density of states electron effective mass.

Solving \(\frac{n_0(n_0 + N_a)}{N_d - N_a - n_0} = \frac{N_C}{g} \exp\left(-\frac{E_d}{kT}\right)\) Equation 4.8 for \(n_0\) gives:

\[
n_0(T) = 2(N_d - N_a) \left[ 1 + \frac{gN_a}{N_C} \exp\left(-\frac{E}{kT}\right) \right]
\]

\[
+ \left\{ \left[ 1 + \frac{gN_a}{N_C} \exp\left(\frac{E_d}{kT}\right) \right]^2 + \left[ 4g(N_d - N_a) \right] \exp\left(-\frac{E_d}{kT}\right) \right\}^{-1}
\]

Equation 4.10

Therefore, given the values of \(n_0\) determined from experimental measurements as a function of temperature, the parameters \(N_a, N_d,\) and \(E_d\) can be extracted by fits of Equation 4.8 to the measured data.
4.4.2 Capacitance-Voltage (C-V) Profiling

Along with Hall measurements, C-V profiles can be used to measure the dopant concentration of a sample with the important difference that while the Hall effect measures free carrier concentration of a layer, C-V measures the concentration of fixed charge in the depletion region of a junction, as will be shown in this section. Since the depletion region of a Schottky barrier or a one-sided p-n junction contains a certain amount of fixed charge associated with ionized donors and/or acceptors, the capacitance of the junction can be considered as a parallel plate capacitor; it is simply a function of the area of the junction measured (A), which is fixed, and the width of the depletion region (W):

\[
C = \frac{\varepsilon_0 \varepsilon_s A}{W}
\]

Equation 4.11

Where \(\varepsilon_0\) and \(\varepsilon_s\) are the permittivities of free space and of the semiconductor, respectively. The width of the depletion region, which depends on the applied bias, is well known from basic semiconductor physics:

\[
W = \sqrt{\frac{2 \varepsilon_s \varepsilon_0 (V_{bi} - V)}{q N_{scr}}}
\]

Equation 4.12

Where \(V_{bi}\) is the built-in voltage of the junction, \(V\) is the applied voltage, and \(N_{scr}\) is the doping in the depletion region (space-charge region). The applied voltage shifts the edge of the depletion region thereby changing the amount of charge it contains. Capacitance can be written as:

\[
C = \frac{dQ}{dV}
\]

Equation 4.13

Where \(Q\) is the charge in the depletion region, given by:
\[ Q = qA \int_{0}^{W} N_{SCR} \, dx \quad \text{Equation 4.14} \]

\[ C = qAN_{SCR}(W) \frac{dW}{dV} \quad \text{Equation 4.15} \]

The term \( dW/dV \) can be found from by differentiating \( C = \frac{\varepsilon_{s}\varepsilon_{0}A}{W} \) Equation 4.11 with respect to voltage. Then, solving for \( N_{SCR}(W) \):

\[ N_{SCR}(W) = \frac{C^3}{q\varepsilon_{s}\varepsilon_{0}A^2 dC/dV} \quad \text{Equation 4.16} \]

This result shows how dopant density can be extracted from a C-V profile. A significant note is that a result of measuring with respect to voltage bias is a depth profile of the dopant concentration.

### 4.4.3 Deep Level Transient Spectroscopy (DLTS)

DLTS is a powerful tool first developed in the 1970s that has since become a widely used instrument for investigating electronic states in semiconductor materials [21, 22]. Following the previous discussion on C-V measurements, DLTS is based on the principle that carrier capture or emission by traps located in the depletion region will affect the depletion capacitance of a Schottky diode or pn junction. These processes can be triggered by changing bias conditions to prompt a change in the depletion width of the junction, thereby exposing more or less semiconductor volume to the built-in field of the junction. By analyzing capacitance transients resultant from changes in bias conditions, information regarding trap properties is obtained. To explain this experimental technique more thoroughly, and also to support discussion in subsequent chapters regarding the traps found in photovoltaic materials, first the physics of trapped carriers is briefly reviewed.
Considering a defect in a material interacting with a charge carrier, there are four processes that can take place: electron capture, electron emission, hole capture and hole emission. The rate of electron capture and emission can be given as:

\[
\frac{\partial n_T}{\partial t} \bigg|_{\text{capture}} = c_n p_T n \quad \text{Equation 4.17}
\]

\[
\frac{\partial n_T}{\partial t} \bigg|_{\text{capture}} = -e_n n_T \quad \text{Equation 4.18}
\]

Here, \(n_T\) is the concentration of trapped electrons, \(c_n\) is the electron capture coefficient, \(p_T\) is the concentration of trap states empty of electrons, and \(n\) is the concentration of electrons. Corresponding equations for holes have the same structure. Considering all four processes, the rate of change of the concentration of trapped electrons follows as:

\[
\frac{\partial n_T}{\partial t} = (c_n p_T n - e_n n_T) - (c_p p_T n_T - e_p p_T) \quad \text{Equation 4.19}
\]

Where the first term represents electron processes and the second represents hole processes. In equilibrium, the ratio of the number of trapped electrons to the number of traps \((N_T)\) is given by Fermi-Dirac statistics:

\[
\frac{n_T}{N_T} = \frac{1}{1 + \exp(E_T - E_F / kT)} \quad \text{Equation 4.20}
\]

From detailed balance considerations, for which capture and emission are in equilibrium, and using standard Fermi equations for n and p, the ratio of rate of emission to rate of capture can be determined as a function of trap energy, Fermi energy, and temperature:
\[
\frac{e_n}{c_n} = \exp \left(\frac{E_T - E_F}{kT}\right) \quad \text{Equation 4.21}
\]

Where \(E_T\) is the trap level and \(E_F\) is the Fermi level referenced to the valence band maximum \(E_V\).

\[
\frac{e_n}{c_n} = \exp \left(\frac{E_T - E_F}{kT}\right) \quad \text{Equation 4.21 makes sense physically; if the trap energy level is above the Fermi level, emission must exceed capture. Additionally, capture rates can be defined as:}
\]

\[
c_n = \sigma_n \langle v_{th} \rangle n = \sigma_n \langle v_{th} \rangle N_c \exp \left(\frac{E_F - E_C}{kT}\right) \quad \text{Equation 4.22}
\]

Where \(\sigma_n\) is the capture cross-section and \(\langle v_{th} \rangle\) is the electron thermal velocity.

Combining Equations 4.22 and 4.21, descriptive equations are obtained that clearly show the influence of trap energy level and temperature on the thermal emission rates of electrons and holes:

\[
e_n(T) = \sigma_n \langle v_{th} \rangle N_c \exp \left(-\frac{E_C - E_T}{kT}\right) \quad \text{Equation 4.23}
\]

\[
e_p(T) = \sigma_p \langle v_{th} \rangle N_V \exp \left(-\frac{E_T - E_V}{kT}\right) \quad \text{Equation 4.24}
\]

The goal is therefore to perform a measurement that allows the characteristic values of a trap to be determined explicitly: capture cross-section and activation energy. This can be done with DLTS which relies on the changes in the depletion capacitance, which is:

\[
C_0 = \frac{\varepsilon_s \varepsilon_0 A}{W} = \sqrt{\frac{q \varepsilon_s \varepsilon_0}{2}} \sqrt{\frac{N_{scr}}{V_{bi} - V_{app}}} \quad \text{Equation 4.25}
\]

Where the charge in the depletion region, assuming an n-type region, can be written as:
\[ N_{SCR}(t) = N_D - n_T(t) \]  
Equation 4.26

The concentration of filled trap states is now written explicitly as a function of time due to the nature of the DLTS measurement. A typical DLTS measurement proceeds as such: (1) a quiescent reverse bias is applied to the junction, creating a given depletion width and empty traps within; (2) a fill pulse bias is applied to shrink the depletion width, filling traps with carriers; (3) the fill pulse bias is removed and free carriers are again swept from the depletion region, with the emptying of traps occurring at a rate dependent on carrier emission. This process is depicted in Figure 4.8 (a) and (b). Substituting this time-dependent expression for \( N_{SCR} \) back into Equation 4.24, an expression for \( C(t) \) is obtained:

\[
C(t) = \sqrt{\frac{q \varepsilon \varepsilon_0}{2}} \sqrt{\frac{N_D - n_T(t)}{V_{bi} - V_{app}}} \sqrt{\frac{q \varepsilon \varepsilon_0 N_D}{2(V_{bi} - V_{app})}} \left(1 - \frac{n_T(t)}{N_D} \right) = C_0 \left(1 - \frac{n_T(t)}{N_D} \right)
\]

Equation 4.27

Since the trap concentration will in general be much less than the concentration of donors, a binomial series expansion simplifies this equation to:

\[
C(t) = C_0 \left[1 - \frac{1}{2} \frac{n_T(t)}{N_D} \right]
\]

Equation 4.28

Such that the occupied trap concentration is described as a function of the concentration of donors and the change in capacitance during a DLTS capacitance transient measurement. If the trap is assumed to be completely filled initially, the occupancy over time can be expressed as:

\[ n_T(t) = N_T \exp(-e_n t) \]

Equation 4.29
So that the capacitance transient is defined as a function of an exponential term of the emission coefficient of the given carrier:

\[
\frac{\Delta C(t)}{C_0} \approx \frac{N_t}{2N_d} exp(-e_n t)
\]

Equation 4.30

This equation is the basis of the depletion capacitance-based measurements used in this thesis. The experiment described is shown in Figure 4.8, where the bias conditions are shown in (a) and the resultant diode capacitance in (b). If a sample is measured like this for a range of temperatures, the time constant can be plotted as a function of temperature, as in (c). Selecting a reference time constant, \( \tau_{ref} \), a maximum value of the DLTS signal can be obtained for a given temperature. A series of maximum temperature and reference time constant values allows for an Arrhenius plot of \( \ln(\tau_{ref} T_M^{2}) \) vs. \( T_M^{-1} \) which can be fitted to extract the trap parameters.
4.4.4 Steady State Photocapacitance (SSPC) and Deep Level Optical Spectroscopy (DLOS)

The thermal nature of DLTS and the limits of practical temperature range restrict the measurement to about 1 eV from a bandedge. DLOS provides the means to probe...
deeper states through the optical, rather than thermal, excitation of trapped carriers since sub-bandgap light can induce the emission of a trapped carrier. The optical emission rate of a carrier is:

\[ e^0(hv) = \sigma_{n,p}^0(hv)\Phi(hv) \quad \text{Equation 4.31} \]

Where \( \sigma_{n,p}^0(hv) \) is the optical cross section for electrons and holes and \( \Phi(hv) \) is the photon flux. From this equation it is obvious that the optical cross section, instead of the emission rate, is the characteristic value for a trap, since the photon flux is dependent on the measurement set up. In DLOS experiments, the capacitance transient associated with the optically-stimulated emission of carriers from deep levels is measured as a function of incident photon energy. Information can also be obtained by analyzing the final, steady-state capacitance. The following equations show this, where an n-type sample is again assumed. In the case of optical stimulation of trapped carriers, capture will be insignificant

\[ \frac{\partial n_T}{\partial t} = (cnpTn - ennT) - (cppnT' - eppT') \quad \text{Equation 4.19} \]

This can be written as:

\[ \frac{\partial n_T}{\partial t} = -e_n^0 n_T + e_p^0 p_T = -\sigma_n^0(hv)\Phi(hv)n_T - \sigma_p^0(hv)\Phi(hv)p_T \]

\[ \quad \text{Equation 4.32} \]

Solving this equation for the concentration of filled traps gives the steady state limit, as \( t \to \infty \):

\[ n_{T,SS} = \frac{\sigma_p^0}{\sigma_n^0 + \sigma_p^0} N_T \]

\[ \quad \text{Equation 4.33} \]

Which can then be related to capacitance as:

\[ \frac{\Delta C}{C_{SS}} = \frac{N_T}{2N_D} \frac{\sigma_n^0}{\sigma_n^0 + \sigma_p^0} \]

\[ \quad \text{Equation 4.34} \]
For an n-type material, if the minority carrier optical cross-section ($\sigma_p^o$) goes to zero, the trap concentration can be determined directly from the measured steady-state capacitance. If $\sigma_p^o$ is significant with respect to $\sigma_n^o$, then the trap concentration found in this way is a lower limit on the real concentration. As mentioned previously, a more thorough characterization of deep levels by DLOS requires further study of the capacitance transients themselves. More thorough treatments of these topics are provided in References [22, 23].

4.5 References


Chapter 5

Epitaxy and Characterization of Gallium Phosphide

A key element of the III-V/Si multijunction solar cell is the advanced understanding of the growth space and material characteristics of gallium phosphide, a material whose characteristics have not been thoroughly studied with modern growth techniques. First, due to its close lattice matching to Si, GaP is to be used as the III-V nucleation layer on Si. This requires that a GaP/Si interface and a coherent layer of GaP are in series with the rest of the multijunction device and is thus a critical component. Second, GaAs$_y$P$_{1-y}$ is used as the middle junction of the solar cell as well as the compositionally graded buffer to span the lattice constant difference between the Si substrate/subcell and the middle and top junctions. The study of the growth and material properties of GaP is motivated by the fact that GaP is the lesser studied of the two binary constituents of GaAs$_y$P$_{1-y}$ so that the understanding of the alloy system gains from the expanded knowledge of GaP growth space and electronic properties. Finally, the study of GaP also supports the study of Ga-rich compositions of Ga$_x$In$_{1-x}$P by providing material properties for the binary endpoint allowing a more thorough understanding Ga$_x$In$_{1-x}$P material properties as a function of composition. This chapter discusses the exploration of the GaP homoepitaxial growth space in both the MBE and MOCVD growth systems, resulting in the discovery of a high-temperature step-flow growth mode in MBE which is shown to transfer directly to the MOCVD system, with similar surface morphologies found for equal growth temperatures.
in both systems. Electrical measurements are performed to characterize this new regime of GaP growth and to set a baseline of material parameters which can be used to compare GaP layers grown on different substrates and grown by different growth techniques.

5.1 Introduction

To date, little has been published regarding GaP epitaxy by MBE and MOCVD in terms of optimized epitaxial growth and almost no reports on transport properties and electronic defects of such materials are available. Compared with common III-V materials such as GaAs, InP and GaN, epitaxial GaP is really in its infancy.

That said, GaP does have a rich history of research, development and technological applications that to date have been almost exclusively limited to devices based on either bulk crystals or liquid phase epitaxy (LPE), and this provides context for the epitaxy and characterization studies described in this chapter. Despite its indirect bandgap and low electron mobility, interest in GaP was substantial in the 1960s and 1970s for LED devices where isoelectronic impurities were introduced into its bandgap to induce radiative recombination and visible spectrum lumination [1]. For GaP and GaAs$_y$P$_{1-y}$, introduction of Zn-O centers produced red light emission and were an improvement over previous iterations of red LEDs [1, 2]. Nitrogen was also found to be an excellent candidate as an impurity for both GaP and GaAs$_y$P$_{1-y}$ because it has not only a small activation energy but also a tightly localized potential in real space, meaning that its energy states are spread out in momentum space (an example of the Heisenberg uncertainty principle), making direct carrier transitions possible [3]. Thus, efficient (relative to other technologies of the era) green illumination was possible from GaP crystals. GaP LEDs reached their limit in part because limits on the concentration of nitrogen doping levels were reached and also
because of non-radiative recombination processes that limited internal quantum efficiencies \cite{1, 4}. Efforts were undertaken to characterize these processes, leading to early work on trap levels in GaP, and deep levels related to nitrogen doping \cite{5}, vacancy and antisite defects \cite{6}, silicon \cite{7}, and oxygen \cite{8}, were investigated. Ultimately, GaP-based LEDs based on bulk wafers and LPE were rendered obsolete with the advent of epitaxial growth methods such as molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) in the 1970’s and 1980’s that led to advanced heterojunction and quantum well based technologies, including AlGaAs/GaAs, AlGaInP, and, more recently GaN based devices, which to this day dominate optoelectronic device applications.

In addition to LED applications, GaP also attracted early interest as a candidate material for high temperature electronic applications due to its high band gap and good thermal stability. Reasonable results on electronic devices up to 500°C were achieved \cite[see Ref. 9 and references therein]{9}. As with LEDs, the advent of higher performance semiconductors based on advanced epitaxial growth techniques surpassed GaP-based technologies since the early GaP efforts for electronic devices were also based on either bulk crystals or liquid phase epitaxy (LPE) which are not capable of creating the heterostructure designs needed for high performance devices. Therefore, efforts toward experimental measurement of GaP electronic properties made on bulk and LPE materials, including studies of Schottky barriers \cite{10}, p-n junctions \cite{11}, and carrier doping and mobility studies \cite{12-16}, provide a useful baseline material parameter set with which to compare the high quality epitaxial GaP layers that are discussed in this chapter.

The work described previously in section 3.2 on the growth of GaP films on Si has already resulted in high quality crystalline films and subsequent metamorphic GaAs$_y$P$_{1-y}$
materials and photovoltaic devices. However, aside from a few reports on MBE growth pertaining to surface reconstructions [17-19], dopant incorporation [20], and even potential application for solar cells [21], the range of GaP growth conditions in MBE and MOCVD has not been fully explored. Of greatest impact is determination of the growth temperature range (and therefore V:III beam flux ratio (for MBE) or flow ratio (for MOCVD)) for which outstanding crystal quality can be obtained. This is in large part needed so as to maximize the GaP growth temperature to enable the maximum extend of misfit dislocation gliding at the GaP/Si interface to create the lowest density of threading dislocations at the first layer of the GaAs$_x$P$_{1-y}$ metamorphic buffer on Si. Once determined, the behavior of intentional doping and possible non-intentional creation of defects that can give rise to bandgap states, all must be considered. An entire multi-property optimization is needed so as to determine the ideal growth conditions within the MBE and MOCVD growth phase diagram for GaP epitaxial layers.

5.2 Homoepitaxy of GaP by MBE and MOCVD

This section presents work undertaken to elucidate the relationship between a range of GaP homoepitaxial conditions with the resultant growth mode and post-growth surface morphology. Since a major goal of this work is to aid in directing future experiments on compositionally graded, strain-relaxed layers which are generally found to possess lower dislocation densities with higher substrate growth temperatures, as described in section 3.1, we here explore an atypical (for III-AsP materials) high-temperature MBE growth regime in which ideal step-flow epitaxy of GaP is achieved.
5.2.1 MBE GaP Homoepitaxy

The first key step is to determine the extent of the growth phase diagram for homoepitaxial GaP using MBE. From surface reconstruction studies on gas source MBE, it has been reported that above the GaP congruent sublimation temperature of GaP (687°C), the phosphorous overpressure required to maintain the P-rich (2×4) begins increase exponentially. Studies concerning thin layers of GaP grown on Si have reported the complete desorption of films annealed at temperatures of 750°C under P2 overpressure.

MBE growths reported in this chapter were performed on nominally on-axis, 2 inch diameter GaP(100) substrates. High resolution XRD experiments confirmed the substrate misorientation to be less than 0.2°, with no preferred misorientation direction. Both semi-insulating double-side polished and n-type single-side polished substrates were used, with no difference in surface morphology of subsequent growths observed between the two. To improve heat absorption and enable useful infrared pyrometry temperature measurements in the MBE growth chamber, the substrates were back-coated with 0.5 µm of titanium via electron beam deposition prior to loading. Once loaded into the growth chamber, the native oxide was removed thermally by annealing the substrate to above 630°C under P2 overpressure. Substrate oxide removal was confirmed by a RHEED pattern transformation from a spotty (1×1) pattern to a weak (2×4) pattern. All MBE-grown samples reported here were grown to an epitaxial layer thickness of 0.5 µm at a 0.93 µm/h growth rate (with respect to RHEED intensity oscillation measurements made at 600°C) and were nominally doped \( N_D = 1 \times 10^{17} \text{ cm}^{-3} \) n-type with Si.

Figure 5.1 presents AFM images and surface roughness measurements from a systematic series of MBE-grown samples produced in this study in order to map out a range
of growth temperature and flux ratio conditions. Within this range, the samples grown at 680°C and 16:1 P₂:Ga flux ratio exhibited the best post-growth morphology, with well-ordered steps and 200–300 nm wide terraces free of major islands (consistent with the unintentional misorientation angles measured), indicating a step-flow growth mode. Post-growth RHEED images taken at 600°C (see Figure 5.2) show a sharp, streaky (2×4) pattern, indicating a smooth, well-ordered surface. However, RHEED patterns observed during growth exhibited a slight splitting of the 2× secondary streak (note that all efforts to capture a useable image of this, however, were unsuccessful). This splitting could be the result of diffraction pattern mixing between the (2×4) and some other transient surface reconstruction. Although another example of such a RHEED pattern splitting phenomenon could not be found in the literature, mixed surface reconstructions, and their resulting mixed diffraction patterns, have indeed been reported for GaAs [22].

Several general trends in surface morphology as a function of growth conditions, and insights into the growth physics of GaP, are apparent from Figure 5.1. A 20°C increase in temperature (with the same flux ratio) from the best conditions of this subset (680°C and 16:1 P₂:Ga) resulted in pitting several bi-layers deep. Further temperature increases, or decreases in the P₂:Ga flux ratio, also resulted in significant surface pitting, consistent with high Ga adatom diffusivity and deficient P₂ availability.

Samples grown colder than 680°C still resulted in relatively smooth, stepped surfaces, as seen in the AFM images of Figure 5.1 for growth at 660°C and 640°C, but a significant roughening of the step edges was observed. Additionally, numerous step-height islands are observed, with increasing density and decreasing average area as the temperature is reduced, consistent with a decrease in Ga adatom diffusivity and a transition
toward a layer-by-layer island-coalescence growth mode [23]. Decreasing the P₂:Ga ratio at the lower growth temperatures would most likely improve the surface morphology to some extent, until the temperature is too low to provide sufficient energy for appreciable Ga adatom diffusion, at which point step-flow growth is impossible. Additionally, it is worth noting that the steps in all of the AFM images tend to align perpendicular to the [0\bar{1}1] direction despite the fact that the unintentional substrate offcut directions are varied. This behavior suggests a possible Ga adatom-surface dimer interaction, such as that described for GaAs (Ref. [24]) on the β2(2×4) surface reconstruction, which creates an adatom diffusion anisotropy with respect to the growth surface; an identical reconstruction is also believed to be stable for the P-rich GaP(100) surface [25]. Although not every AFM image displays steps perfectly perpendicular to the [0\bar{1}1] direction, the general trend seems to point toward a natural preference for step flow growth in this direction.
Figure 5.1: AFM images of MBE-grown homoepitaxial GaP over a range of substrate growth temperatures and P₂:Ga flux ratios. The x-axis represents substrate growth temperature and the y-axis represents the P₂ to Ga flux ratio. Each sample was measured on a 5 µm × 5 µm scale with an average z-range of 0 to 2.5 nm. Root-mean-square surface roughness (Rₐ) measurements are given for each image.
Figure 5.2: Post-growth RHEED pattern images, in the (a) [110] and (b)[1 1 0] directions, showing a streaky 2×4 pattern for a typical homoepitaxial GaP growth performed at 680°C and 16:1 P₂:Ga flux ratio.

5.2.2 MOCVD GaP Homoepitaxy

It is of great interest to explore the transition from MBE to MOCVD for several reasons. First, it is well known that there is an upper limit on the growth temperature of P-containing compounds in the UHV environment of MBE. GaₙIn₁₋ₙP, a key component of the multijunction solar cell of interest in this work, is limited by In loss issues [26] and other alloys are limited by the smaller achievable V:III ratios achievable in MBE. Second, MOCVD systems in general, and certainly here at OSU, are able to use larger wafer sizes and are capable of higher growth rates and higher throughput. Traditionally, the commercial production of high efficiency triple junction solar cells utilizing Ga₀.₅₁In₀.₄₉P subcells has been dominated by MOCVD [27], though either growth method is capable of extremely high efficiency devices.
To this end, a more limited, exploratory study of GaP homoepitaxial growth conditions was performed via MOCVD using the results of the MBE-grown samples as a general guide. MOCVD growth of GaP was performed at a pressure of 115 Torr. The carrier gas used was H\textsubscript{2} at a flow rate of 6 slpm while trimethylgallium (TMGa) and phosphine (PH\textsubscript{3}) were used as the gallium and phosphorus precursors, respectively. MOCVD-grown samples were not intentionally doped. MOCVD V:III ratios quoted are a ratio of the precursor molar flows.

An optimal step-flow morphology (see Figure 5.3 (a)), with very regular and straight step edges and terrace widths, was found for MOCVD GaP homoepitaxy at a growth temperature of 725°C, using a PH\textsubscript{3}:TMGa flow ratio of 100:1, a nominal growth rate of 2 µm/h and on-axis substrates, identical to those used in the MBE study. In a simple, non-optimized exploratory attempt to recreate these conditions via MBE, a similarly smooth step-flow morphology, with even straighter step edges than the 680°C samples (see Figure 5.3 (b)), was achieved at 725°C with a P\textsubscript{2}:Ga flux ratio of 30:1. The observed (2×4) RHEED pattern for these conditions appeared to be identical to that of the lower temperature growths. The P\textsubscript{2} flux necessary to maintain a high-quality step-flow growth morphology was found to rapidly increase above 680°C, most likely due to an increased rate of GaP thermal decomposition and subsequent P\textsubscript{2} and Ga desorption, and approaches the sort of V:III ratios often seen in MOCVD growth. It is thus evident that smooth, two-dimensional, step-flow growth is indeed possible via MBE at atypically high growth temperatures as long as the P\textsubscript{2} availability is sufficient to overcome the potential for detrimental Ga adatom clustering and droplet formation. The nearly identical surface morphologies achieved for MOCVD and MBE-based growths at this atypically high
growth temperature (with respect to MBE) present a rarely seen convergence of growth conditions for these two disparate growth techniques.

Figure 5.3: Comparison of AFM measured surface morphologies for (a) MOCVD-grown and (b) MBE-grown homoepitaxial GaP, grown at a substrate temperature of 725°C and V:III ratios of 100:1 and 30:1, respectively.

Figure 5.3: Comparison of AFM measured surface morphologies for (a) MOCVD-grown and (b) MBE-grown homoepitaxial GaP, grown at a substrate temperature of 725°C and V:III ratios of 100:1 and 30:1, respectively.
Note that with the increasing temperature, one might expect a reduced GaP growth rate due to increasing Ga desorption, as observed in other materials systems [28]. However, cross-sectional scanning electron microscopy (SEM) thickness measurements of a GaP test sample grown at 680°C and 16:1 P₂:Ga indicated no reduction of GaP growth rate under these conditions. It is nonetheless worth noting that such a reduction may exist at the 725°C growth temperature [29], for both MBE and CVD-grown samples.

5.3 Electrical Transport Studies of MBE-Grown GaP

As mentioned in the introduction of this chapter, there are limited to no careful studies reported on electrical properties of GaP grown by either MBE or MOCVD on any type of substrate. The only body of work on GaP in this area occurred decades ago mostly on LPE and bulk substrate materials. Therefore, research geared toward elucidating the electrical properties of the GaP films grown by MBE and MOCVD, and more specifically under the growth conditions just described, is needed as this is crucial to the success of III-V devices grown on GaP/Si virtual substrates.

5.3.1 Background

The application of the temperature dependent doping concentration equation, Equation 5.1, whose parameters were defined in Section 4.4.1, is complicated by the nature of the GaP band structure.

\[
\frac{n(n+N_A)}{N_D-N_A-n} = \frac{N_C}{g} \exp \left( -\frac{E_D}{kT} \right) \quad \text{Equation 5.1}
\]
One of the components of Equation 5.1, the conduction band density of states, $N_C$, is actually not well known for GaP due to uncertainty in the conduction band density of states effective mass of GaP. With detailed luminescence measurements [30], GaP was shown to have a “camel’s back” structure around the minimum energy of its indirect, $\chi$-valley bandgap characterized by minima at $0.96K_{100}$ with an energy difference between the minima and the exact zone boundary of about $\Delta E = 3.2$ meV (Figure 5.4). This results in a temperature- and impurity concentration-dependent effective mass.

$$N_C = N'_C \times \left( \frac{T}{T_{3/2}} \right)^{3/2} = 2 \left( \frac{2\pi m^* kT}{\hbar^2} \right)^{3/2} \quad \text{Equation 5.2}$$

$$m^*_C = v^{2/3}(m^*_t m_l)^{1/3} \quad \text{Equation 5.3}$$

Effective mass is given by Equation 5.3, where $v$ is the number of equivalent valleys ($v = 6$ for the camel’s back structure of GaP), $m_t$ is the transverse effective mass and $m_l$ is the longitudinal effective mass. The transverse effective mass ($m_t$) is not sensitive to the camel’s back structure and has a value derived from cyclotron resonance of $m_t \approx 0.25m_0$, which is generally accepted in the literature (see Table 5.1). The longitudinal mass ($m_l$) has a wide range of reported values in the literature. Several are listed in Table 5.1 along with the corresponding references. Some of the values listed are data derived from measurements such as cyclotron resonance and faraday measurements, some are inferred from Schrodinger equation-based calculations, and some are values used by authors in Hall effect measurements with theoretical arguments given for the value chosen.
Figure 5.4: a) Band structure of GaP showing its indirect bandgap at the X-valley. b) Enlarged view of the X-valley bandgap minimum showing the camel’s back structure with minima located at some distance (0.93) away from K_{100}. 
Table 5.1: List of effective masses and reduced density of states ($N_c' \times T^{3/2} = N_c$)

<table>
<thead>
<tr>
<th>Source</th>
<th>Method</th>
<th>$m_t$</th>
<th>$m_l$</th>
<th>$m_c^*/m_0$</th>
<th>$N_{c'}$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dean [31]</td>
<td></td>
<td>0.25</td>
<td>2.92</td>
<td>1.18</td>
<td>$6.19 \times 10^{15}$</td>
</tr>
<tr>
<td>Kasami [32]</td>
<td>Schrodinger Approximation</td>
<td>0.21</td>
<td>1.15</td>
<td>0.77</td>
<td>$3.26 \times 10^{15}$</td>
</tr>
<tr>
<td>Podor [13]</td>
<td>Hall Effect</td>
<td>0.25</td>
<td>2.5</td>
<td>1.79</td>
<td>$1.16 \times 10^{16}$</td>
</tr>
<tr>
<td>Vink [33]</td>
<td>Hall Effect</td>
<td>--</td>
<td>--</td>
<td>1.44</td>
<td>$8.34 \times 10^{15}$</td>
</tr>
<tr>
<td>Suzuki [34]</td>
<td>Cyclotron resonance</td>
<td>0.254</td>
<td>2.032</td>
<td>1.06</td>
<td>$5.27 \times 10^{15}$</td>
</tr>
<tr>
<td>Leotin [35]</td>
<td>Cyclotron resonance</td>
<td>0.25</td>
<td>5.0</td>
<td>1.41</td>
<td>$8.09 \times 10^{15}$</td>
</tr>
<tr>
<td>Siegel [15]</td>
<td>Hall Effect</td>
<td>--</td>
<td>--</td>
<td>1.09</td>
<td>$5.49 \times 10^{15}$</td>
</tr>
</tbody>
</table>

The significance of this is that $N_c$ in the above equation should actually vary with temperature and doping concentration. This couples with an already experimentally verified feature of temperature-varying Hall effect measurements of any material system: that ionization energy is routinely found to be concentration dependent despite the fact that the optically measured ionization energy is concentration independent [36]. A theory based on an ionized electron distribution was formulated by Monecke et al. [36] and tested experimentally for n-type GaP by Siegel et al. [15] who compare the use of the concentration-dependent model ($E_D(n)$ - Equation 5.5) to that of the standard equation, Equation 6.4:

$$E_D = E_{D_0} - \alpha N_A^{1/3}$$

Equation 5.1
In these expressions, $E_D$ is the thermal ionization energy measured by Hall effect measurements, $E_{D0}$ is the thermal ionization energy in the infinite dilution limit and $\alpha$ is a proportionality factor. $E_{D0}$ for Si in GaP, as measured by optical methods, has a value around 82-85 meV [13, 15, 33]. The results indicate that the density of states ($N_C$) and the concentration of acceptors ($N_A$) in Equation 5.1 are quite sensitive to the choice of model – varying by up to a factor of three between the two models. This sensitivity is assumed to be due to the $E_D(n)$ dependence and not to a concentration dependence of the density of states effective mass [15]. While the authors admit that they cannot rule out effects from the concentration-dependent effective mass, especially due to the complicated nature of the GaP band minima, their data show that for the standard model, the density of states has a strong dependence on doping concentration whereas for the adjusted $E_D(n)$ model this dependence disappears. Despite all this, other experiments on temperature-varying Hall effect measurement on GaP:Si utilizing the standard model have found values for $E_{D0}$ consistent with those measured optically, albeit with a significantly different value for $m^*$ and $N_C$ (see Table 5.1) [13]. For the following analysis, fitting was done using the standard model, but allowing $N_C$ to vary as a fit parameter between $9.2 \times 10^{14}$ and $3.0 \times 10^{15}$ cm$^{-3}$, which should account for the effects of the temperature dependence of $E_D$, as concluded in Ref. [15]. Equation 5.4 was not used because it results in the further complication of an already complicated fitting procedure, where $E_{D0}$ and $\alpha$ act on $E_D$ with the same functional dependence and five free parameters must be fit. It should also be noted that the Hall factor for this analysis is chosen to be 1 (arguments for this selection for n-GaP are given in [13]). Results obtained in the following section are compared to the two detailed studies of Hall
effect measurements on Si-doped GaP films cited frequently throughout this section: Podor et al. [13] and Siegel et al. [15]. The study by Podor tested GaP samples grown by liquid phase epitaxy (LPE) and liquid encapsulated czocharlski (LEC). Samples tested by Siegel et al. were grown by synthesis from solute diffusion (SSD). Our efforts are the first, to our knowledge, using MOCVD and MBE. Crystals grown in the liquid-phase epitaxial methods are grown at much higher temperatures than MOCVD or MBE allow. GaP crystals and layers are generally grown in the range of 800°C to 1100°C for SSD and LPE and around 1470°C (the melting temperature of GaP) for LEC [37]. These high growth temperatures provide for conditions much closer to thermodynamic equilibrium (at thermodynamic equilibrium for LEC), and thus is very different from MBE and also from MOCVD, both of which can be significantly dictated by kinetic processes, especially MBE.

5.3.2 Dopant Activation, Mobility and Compensation

Temperature-dependent Hall effect measurements were performed on three n-type (doped with Si) GaP samples of nominal doping levels $5 \times 10^{16}$, $5 \times 10^{17}$, and $5 \times 10^{18}$ cm$^{-3}$ grown on on-axis, semi-insulating GaP(100) wafers after fabricating Van der Paw structures for Hall measurements. The layer thicknesses were 1.25, 1.0 and 0.5 µm respectively. Growth was carried out by MBE under the step-flow growth conditions discussed in the previous section: A growth temperature of 680°C and a V:III flux ratio of 16:1. GaP contact layers 100 nm thick and doped $1 \times 10^{19}$ cm$^{-3}$ were used on the samples doped $5 \times 10^{17}$ and $5 \times 10^{16}$ cm$^{-3}$ to maintain good ohmic contact. After contacts were formed, the contact layer was dry etched using a SiCl$_4$/BCl$_3$ chemistry in an inductively-coupled plasma reactive ion etch system. Ohmic contacts of Ni-Ge-Au-Ni-Au metal stacks (50/250/1,000/200/1,000Å) were deposited on the corners of 8 × 8 mm samples after
cleaning in a 4:1 H₂O:HCl oxide etch. After deposition, the contact stack was annealed for five minutes at 450°C in 10 sccm N₂.

Figure 5.5: Plot of GaP doping concentration measured by Hall compared to GaAs-based doping calibration for Si sublimation cell temperature.

Room temperature carrier concentrations are shown in Figure 5.5 plotted vs. the GaAs-based doping calibration curve generally used to determine Si dopant cell temperatures for growths in the MBE system. The figure shows a close relationship between the doping of GaP and GaAs, with the exception of the highest doping level where the GaP doping level was measured to be 3.36×10^{18} cm⁻³, significantly below the nominal
doping level of \(5 \times 10^{18}\) cm\(^{-3}\). This difference is likely due to the difference in growth temperature; the standard GaAs sample, which is periodically grown for calibration of the MBE system, was grown with a substrate temperature of 600°C, colder than for the GaP sample. Si is well known to be an amphoteric dopant in III-V materials when present in large concentrations [38]. For Si-doped GaAs, the maximum achievable free carrier concentration from Si dopants is smaller for higher growth [39]. Thus, we see to what approximation the GaAs-based Si dopant calibration is valid for GaP as grown in this study.

Figure 5.6: Log of free carrier concentration vs. temperature for three Si-doped GaP samples of nominal doping levels \(5 \times 10^{16}\), \(5 \times 10^{17}\), and \(5 \times 10^{18}\) cm\(^{-3}\). The red curves represent fits of Equation 5.1 to the measured data with the corresponding extracted parameters shown in Table 5.2.
Results from temperature-varying Hall effect measurements are shown in Figure 5.6 for films of different levels of Si n-type doping along with the corresponding fits of Equation 5.1. Each data point represents the average value of 22 measured field points stepped from 500 Gauss to 1.1 Tesla. Extracted parameters from the fits are given in Table 5.2, but prior to discussion concerning the fits, several insights can be gained qualitatively from the plots. First, it is apparent that the samples are not quite fully ionized at 300K. This is not surprising due to the large ionization energy of Si donors in GaP, ~85 meV (reported for GaP grown by VPE and measured by both optical and Hall effect measurements [13, 15, 33, 40]). Second, carrier freeze out occurs as expected for the 5×10^{16} and 5×10^{17} cm^{-3} doped samples where the temperature becomes too low to allow appreciable thermal ionization of electrons from Si donors. For the highly doped sample, measured carrier concentrations above 1×10^{17} cm^{-3} persist to 50K, indicating a conduction mechanism through the impurity band due to the close proximity of donor atoms to one another. This sample therefore violates the assumptions of the model of Equation 5.1 which require a non-degenerate semiconductor whose conduction is dictated solely by the thermal ionization of carriers to the conduction band. For GaP, a doping concentration of 5×10^{18} cm^{-3} puts the Fermi level well within 3kT of the conduction band, the general guideline for degenerate doping in semiconductors. Nevertheless, the data for these three doping values were fitted to obtain estimated parameters, noting that 2 of the three doping values used behaved in a manner consistent with the model.

The data points of Figure 5.6 were fitted using Origin® to Equation 5.1. Parameters for the fits are given in Table 5.2 with values given for N_D, N_A, E_D, and the reduced density
of states, $N_C'$. Values for $N_A$ and $E_D$ are important because they are the parameters used in the model to estimate $E_{D0}$. Figure 5.7 plots $E_D$ vs. $N_A^{1/3}$ for the data found in this study compared with the data from Ref. [13] and Ref. [15]. Error bars for the data points found in this study correspond to standard errors from the fitting procedure of around 20-40% for $N_A$ and 5% for $E_D$, as is typical for fits of this model to experimental data [13, 15]. These errors suggest what is known to be true: Large sample sizes are necessary to reduce the error in the parameters of interest for these types of analyses. Nonetheless, Figure 5.7 shows that the data obtained for MBE-grown GaP do indeed line up well with the literature data and suggest a thermal ionization energy for Si in GaP of around 87 meV, agreeing better with the results of Siegel et al. [15] than with Podor et al. [13], which makes sense given the fact that $N_C'$ was allowed to vary from $9.2 \times 10^{14}$ to $3.0 \times 10^{15}$ cm$^{-3}$, as the model from Siegel suggests. The values extracted for $N_C'$ agree quite well with the data shown in the reference with $N_C'$ increasing with $N_D^{1/3} - N_A^{1/3}$.

The fit for the highest doped sample was performed over only the six highest temperature points where the data appear to exhibit a thermal ionization roll-off behavior. The fit returned what appear to be reasonable values, but standard errors of over 100% for every parameter indicate that the data cannot be trusted and were subsequently left out of Figure 5.7. This magnitude of error is not a surprise due to the deviation away from a purely thermally ionized carrier conduction mechanism.
Table 5.2: Parameters extracted from fits of Equation 5.1 to temperature-varying dopant concentration measurements for each of the three nominal n-type dopant levels. R² values describing the goodness of fit are also provided.

<table>
<thead>
<tr>
<th>Nominal N_D (cm⁻³)</th>
<th>5×10¹⁸</th>
<th>5×10¹⁷</th>
<th>5×10¹⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sims Si (cm⁻³)</td>
<td>7.3×10¹⁸</td>
<td>7.8×10¹⁷</td>
<td>8.5×10¹⁶</td>
</tr>
<tr>
<td>n (cm⁻³) (300K)</td>
<td>3.36×10¹⁸</td>
<td>5.09×10¹⁷</td>
<td>5.70×10¹⁶</td>
</tr>
<tr>
<td>R²</td>
<td>0.9991</td>
<td>0.9992</td>
<td>0.9998</td>
</tr>
<tr>
<td>E_D (meV)</td>
<td>39.3</td>
<td>79.6</td>
<td>81.4</td>
</tr>
<tr>
<td>N_D (cm⁻³)</td>
<td>7.4×10¹⁸</td>
<td>9.3×10¹⁷</td>
<td>6.6×10¹⁶</td>
</tr>
<tr>
<td>N_A (cm⁻³)</td>
<td>3.6×10¹⁷</td>
<td>3.7×10¹⁵</td>
<td>1.8×10¹⁵</td>
</tr>
<tr>
<td>N_C'(cm⁻³)</td>
<td>3.0×10¹⁵</td>
<td>3.0×10¹⁵</td>
<td>2.0×10¹⁵</td>
</tr>
</tbody>
</table>
Portions of these three GaP films were measured by SIMS at the National Renewable Energy Lab. The results for the Si concentration are plotted in Figure 5.8 and average values for the Si concentration measured are given in Table 5.2. The first 100nm of the sample with nominal dopant concentration of $5 \times 10^{17} \text{ cm}^{-3}$ shows the contact layer grown to make good ohmic contact to the film. The free carrier concentration ($n$) measured by Hall together with the results of the SIMS measurements give a good estimate of the
combined effects of compensation and incomplete ionization. For the samples with nominal doping $5 \times 10^{16}$ and $5 \times 10^{17}$ the ratio of free carrier concentration ($n$) to SIMS-measured Si concentration ([Si]$_{\text{SIMS}}$) are 0.65 and 0.67, respectively. These ratios are due primarily to the incomplete ionization of the Si donors at room temperature as suggested both qualitatively by the slope of the data round 300K as well as by the model showing a relatively low concentration of compensating acceptors. Extending the fitted curves to higher temperature shows the donors to reaching 95% ionization by 400K.

Figure 5.8: Secondary ion mass spectroscopy (SIMS) measurements of three GaP samples of nominal Si doping $5 \times 10^{16}$, $5 \times 10^{17}$, and $5 \times 10^{16}$ cm$^{-3}$. 

Figure 5.8: Secondary ion mass spectroscopy (SIMS) measurements of three GaP samples of nominal Si doping $5 \times 10^{16}$, $5 \times 10^{17}$, and $5 \times 10^{18}$ cm$^{-3}$. 

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The ratio of \( n \) to \([\text{Si}]_{\text{SIMS}}\) for the highest doped sample is 0.46. This indicates significant levels of autocompensation, where the free carrier concentration is reduced either by Si atoms occupying P sites rather than Ga sites (SiP), which results in an acceptor level, by SiP - SiGa nearest neighbor pairs, which are electrically neutral, or by defects trapping electrons such as the [Si-X] defect found in GaAs, where it is believed to be associated with Ga vacancies [41]. An additional note: As mentioned previously, the fitted data are not trustworthy for the highest doped sample, and the close correlation of \( N_D \) with the measured SIMS concentration shown in Table 5.1 may indeed be coincidental and should be taken as such.

### 5.3.3 Hall Mobility

The values and behavior of the measured electron mobilities shown in Figure 5.9 compare well with past studies of electron mobility in LPE-grown GaP:Si [16] and solution grown GaP:Te [14, 37]. Highest measured mobilities here are 155 cm\(^2\)/Vs at room temperature and 2,430 cm\(^2\)/Vs at 50K. The shape of the mobility vs. temperature curves suggests that phonon scattering is the primary scattering mechanism for the lower doped samples (\(5 \times 10^{16}\) and \(5 \times 10^{17}\) cm\(^{-3}\)), where mobility increases with falling temperature and reduced phonon interactions. The highest doped sample shows a much lower overall mobility and its fundamentally different character shows that impurity scattering is the dominant scattering mechanism, correlating with the carrier concentration measurements which showed an impurity donor concentration large enough to induce impurity band conduction.
Figure 5.9: Electron Hall mobility vs. temperature for three Si-doped GaP samples with SIMS-measured doping levels of $8.5 \times 10^{16}$, $7.8 \times 10^{17}$, and $7.3 \times 10^{18}$ cm$^{-3}$.

5.4 DLTS Measurements of Au Schottky Diodes on MBE-GaP

In order to continue the exploration of electronic material quality and to investigate the possible presence of bandgap states that may contribute to the carrier compensation, Au/n-GaP Schottky diodes were fabricated to facilitate DLTS measurements on GaP films grown under the 680°C, 16:1 MBE growth conditions previously described. As mentioned earlier in this chapter, the early successes of GaP LEDs spurred research efforts toward the
electrical characterization of GaP. This included characterization by DLTS, the majority of which was performed on material grown by VPE, LPE, LEC, or SSD [5-8, 42-45], with only one considering layers grown by MOCVD [46]. The need for additional work on the nature of deep levels in GaP is clear.

5.4.1 Schottky Diode Characterization

Figure 5.10 presents the Au-GaP Schottky diode test structure used to perform DLTS. A 0.75 µm thick layer with a nominal dopant concentration of $1 \times 10^{16}$ cm$^{-3}$ was grown on a semi-insulating (100) GaP substrate. A highly doped lateral conduction layer grown underneath the lightly doped test layer was used to make back-side ohmic contact. A portion of the sample was etched with SiCl$_4$/BCl$_3$ chemistry to reveal the highly doped layer in order to make ohmic contact using the same metal contact stack as for the Hall samples.
Figure 5.10: Schematic representation of GaP DLTS structure. A highly doped conduction layer is grown first on a SI GaP substrate in order to make backside ohmic contact to the low-doped test layer.

Figure 5.11 (a) shows a typical room temperature I-V curve obtained from this structure exhibiting extremely low reverse bias leakage current and an extremely strong rectifying behavior. Above about 1V series resistance, effects dominate the forward bias current. The very low reverse leakage current suggests an excellent candidate for capacitance-voltage-based spectroscopy measurements and the $C$-$V$ measurement data are shown in Figure 5.11 (b). The plot of ionized donor concentration vs. depletion width shows a constant doping concentration of just below $1 \times 10^{16}$ cm$^{-3}$ and that a reverse bias of -2.0 V results in a depletion width of 0.69 µm.
Figure 5.11: (a) Current density vs. voltage for a .04 mm² Au-GaP Schottky diodes for an n-type $1.5 \times 10^{17}$ cm⁻³ doped GaP film. (b) C-V profile with the extracted charge density vs. depletion depth in the inset. As denoted in the plot, a reverse bias of -2.0 V (used for subsequent DLTS measurements) forms a depletion depth of 0.69 µm within the lightly doped $n$-GaP layer.
5.4.2 DLTS (Deep Level Transient Spectroscopy)

A quiescent reverse bias of -2.0 V and a fill pulse of 0.0 V for a duration of 10 ms were used for the DLTS measurements. The capacitance transients were measured and recorded within the temperature range of 77K to 400K and DLTS spectra were acquired through boxcar analysis of transients by using rate windows spanning from 1000 to 0.8 s\(^{-1}\).

DLTS spectra are presented in Figure 5.12 along with plots of the associated Arrhenius analyses, as introduced in Chapter 4, whose extracted data are listed in Table 5.3. The measurements revealed seven distinct deep levels whose thermal ionization energies and capture cross-sections have been extracted from the Arrhenius analyses [47] and given in Table 5.3.
Figure 5.12: (a) DLTS spectrum for n-GaP Schottky diode using -2.0V quiescent reverse bias and 0.0V filling pulse for 10 ms. (b) Arrhenius plots of the DLTS data for deep levels.
Table 5.3. Table of activation energy, capture cross-section, and concentration of deep levels in MBE grown n-GaP layer

<table>
<thead>
<tr>
<th>$E_C - E_T$ (eV)</th>
<th>0.20</th>
<th>0.23</th>
<th>0.36</th>
<th>0.54</th>
<th>0.66</th>
<th>0.76</th>
<th>0.94</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_n$ (cm$^2$)</td>
<td>5×10$^{-13}$</td>
<td>6×10$^{-16}$</td>
<td>9×10$^{-14}$</td>
<td>5×10$^{-15}$</td>
<td>6×10$^{-14}$</td>
<td>4×10$^{-14}$</td>
<td>8×10$^{-14}$</td>
</tr>
<tr>
<td>$N_T$ (cm$^{-3}$)</td>
<td>1.2×10$^{13}$</td>
<td>7×10$^{13}$</td>
<td>1×10$^{13}$</td>
<td>2×10$^{13}$</td>
<td>9×10$^{12}$</td>
<td>1.2×10$^{13}$</td>
<td>1.2×10$^{13}$</td>
</tr>
</tbody>
</table>

The concentration of the dominant deep level, with an activation energy of $E_C - 0.23$ eV, is 7×10$^{13}$ cm$^{-3}$ with a capture cross-section ($\sigma_n$) of 6×10$^{-16}$ cm$^2$ in the infinite temperature limit, as determined from the Arrhenius analysis. This level has been reported previously as the dominant level in GaP material grown by VPE measured by DLTS, and as such has received far more research effort than other levels [7, 42-45]. Evidence has suggested that it is related to phosphorous vacancies; the variation of the trap concentration with substrate temperature was found to correspond to the calculated phosphorus vacancy concentration dependence on temperature [44]. It also has been found to depend upon total Si doping concentration, therefore theorized by others to be a $V_P – Si_{Ga}$ complex [7, 45].

While reports of this level in the literature often involve samples not doped with Si, Si is the main background impurity in GaP layers grown in the vapor phase due to hydrogen reactions with quartz apparatus typical in VPE growth chambers [7]. Skazochkin et al. [7] studied the correlation between the background Si concentration and the concentration of $(E_C – 0.23$ eV). A comparison of their data and the measurement made in this work is shown in Figure 5.13. Assuming the $V_P – Si_{Ga}$ complex model for this trap, the data would suggest a smaller concentration of P vacancies for the MBE growth conditions used here.
than for that of the VPE samples described. For now, this sort of conclusion may be taken only as conjecture. This finding does, however, show definitively that the concentration of this electron trap in samples grown by MBE under these conditions is far less than that for VPE-grown samples with similar Si concentration.

Figure 5.13: Plotted \((E_C - 0.23 \text{ eV})\) trap concentration vs. Si concentration from the measurement described in this work compared with data from Reference [7].

The remaining levels seen by DLTS of these MBE samples are similar in activation energy to some found in earlier studies, but capture cross-section values tend not to agree.
These levels have not received a high level of scrutiny or dedicated experiments to relate a physical source.

A level similar to \((E_C - 0.36 \text{ eV})\) measured in this work was reported in Ref. [45] \((E_C - 0.39 \text{ eV})\) where it was compared to the \((E_C - 0.45 \text{ eV})\) level which is frequently reported in nitrogen-doped GaP [44, 48]. This difference in activation energy was attributed to a complex involving Si and N [45]. A capture cross-section between \(6 \text{ and } 40 \times 10^{-15} \text{ cm}^2\) was reported in Ref. [45]. In this work the capture cross-section was determined to be \(9 \times 10^{-14} \text{ cm}^2\).

Levels approximating to those measured in this work at \((E_C - 0.54 \text{ eV}), (E_C - 0.66 \text{ eV}), (E_C - 0.76 \text{ eV}), \text{ and } (E_C - 0.94 \text{ eV})\) were found in References [42], [7, 46], [43], and [43] respectively, but were not broadly investigated or discussed in those works. When given, the capture cross sections for these levels are different by orders of magnitude. Therefore these levels cannot be correlated to those found in previous studies. This highlights the lack of information regarding defects in GaP and the need for further work, especially in MBE and MOCVD since these were all done by Chloride VPE. \(E_C - 0.94 \text{ eV}\) is similar to one found in Reference [43] and was ascribed by those authors to a complex formed around oxygen atoms incorporated in the crystal. However, it is important to note that in our studies, the concentrations of these various traps are very low, as seen in Table 5.3. Thus, their specific role is not expected to be large.

### 5.5 Summary

The introduction to this chapter established the motivation for working on GaP, especially as grown by MBE and MOCVD, from a historical context. As devices
incorporating GaP/Si virtual substrates and GaAs\textsubscript{y}P\textsubscript{1-y} and Ga\textsubscript{x}In\textsubscript{1-x}P metamorphic layers such as multi-junction solar cells become more prevalent in their development, the properties of epitaxial GaP layers become ever more important both to optimize future vertical device structures in which the GaP is the critical layer that allows for integration with Si as well as to improve the understanding of the binary endpoint of the two critical ternary alloys. The results presented in this chapter demonstrate that step-flow growth for homoepitaxial GaP via both MBE and MOCVD is obtainable. These were the first such reports for GaP epitaxy by any growth method. Very smooth and well-ordered surface morphologies offer both a crossover point for the two growth methods as well as a high temperature growth regime for which high quality metamorphic GaAs\textsubscript{y}P\textsubscript{1-y} growth may be anticipated. Additionally, the results described herein provide great promise for achieving high quality graded layers on GaP/Si by both growth methods and highlight the potential of GaP to fulfill its promise to facilitate high quality III-V devices on Si substrates.

With regard to the high temperature growth of metamorphic GaAs\textsubscript{y}P\textsubscript{1-y}, growth of GaAs at 680°C was also investigated and very smooth, step-flow morphology growth surfaces were also achieved for GaAs layers grown by MBE (Figure 5.14). Just as for GaP, this is a growth condition far away from the typical conditions used for GaAs, which are typically around 600°C. From this we observe that both binary endpoints of the GaAs\textsubscript{y}P\textsubscript{1-y} material system are able to be grown at higher temperatures than previously thought (for MBE), and as such lower densities of threading dislocations are expected for GaAs\textsubscript{y}P\textsubscript{1-y} step-graded buffers.
Figure 5.14: AFM measured surface morphology for GaAs grown by MBE, showing a similarly smooth, well-ordered surface and offering promise for similar high-quality growth of GaAs$_x$P$_{1-y}$ layers.

GaP films grown under the same conditions were analyzed by Hall effect measurements showing a Si dopant activation energy in good agreement with GaP films grown in the past. Mobility measurements compared well to those in the literature measured for samples by melt-grown methods which are known to produce a high crystalline quality. DLTS measurements were performed using gold Schottky barriers and revealed seven majority carrier electron traps in the n-type GaP films, all with concentrations below $1 \times 10^{14}$ cm$^{-3}$, providing a baseline for future work, including a comparison of DLTS measurements for MBE and MOCVD-grown GaP films for which preliminary data is presented in Chapter 8 – Conclusions and Future Work.
5.6 References


Chapter 6

Growth and Characterization of MBE-Grown Ga$_{0.57}$In$_{0.43}$P Solar Cells

6.1 Introduction

Recent work in this group has advanced GaAs$_y$P$_{1-y}$ solar cell technology on Si substrates using graded GaAs$_y$P$_{1-y}$/GaP/Si metamorphic buffers, establishing the viability of III-V solar cell technology on Si substrates [1]. Demonstration of high quality single junction top cell devices is an important next step toward realizing the full triple junction device. The pairing of the appropriate top junction to complete this triple-junction design necessitates Ga$_x$In$_{1-x}$P at compositions that are Ga-rich and tensile mismatched with respect to the GaAs lattice constant.

Currently, top cell junctions are a limiting factor in improving the efficiencies of III-V multijunction solar cells. Top cell bandgaps have traditionally been limited to that of Ga$_{0.51}$In$_{0.49}$P lattice-matched to GaAs (1.8-1.9 eV, depending on ordering). With the lattice-matched, Ge-based triple junction approaching its practical limits of efficiency [2, 3], the exploitation of more junctions and better partitioning of the solar spectrum are needed to continue efficiency improvements. To accomplish this, subcells with bandgaps larger than 1.9 eV are needed.
This composition was chosen to provide the 1.95 eV bandgap material that is required for a triple junction solar cell based on Si operating under the AM1.5G spectrum, as discussed in the introduction of this thesis.

In this chapter, we explore the design of Ga-rich Ga$_{x}$In$_{1-x}$P solar cells on tensile-graded GaAs$_{y}$P$_{1-y}$ buffers grown on GaAs substrates as well as on compressive-graded GaAs$_{y}$P$_{1-y}$ buffers grown on GaP and Si substrates. After a discussion on the growth parameters of Ga$_{0.57}$In$_{0.43}$P, descriptions of experiments performed on Ga$_{0.57}$In$_{0.43}$P solar cells grown on tensile-graded buffers on GaAs substrates are presented. The use of tensile-graded buffers grown on GaAs facilitates a low-TDD baseline with which to compare devices grown on compressive-graded buffers on GaP and Si substrates and also enables a greater throughput of experiments than for cells grown on the latter. Section 7.4 then presents solar cells grown on compressive-graded buffers on GaP and Si substrates. The effects of moving from GaAs to Si, and the corresponding increase in threading dislocation density (TDD), are tested by a series of measurements, including DLTS and DLOS.

6.2 Ga$_{0.57}$In$_{0.43}$P Growth Conditions

Growth of InP-based compounds by MBE is well-known to require low growth temperatures [4-7], due to the apparent escape of In from the crystal due to the thermal desorption of P resulting in the formation of In droplets on the surface [7]. Above about 500°C, the incorporation efficiency of In drops dramatically and alloy composition control becomes infeasible [5, 7]. Studies have suggested that the optimal temperature for growth of Ga$_{0.51}$In$_{0.49}$P is close to this thermal decomposition point of 500°C [8]. This, along with the fact that the lower limit of the infrared pyrometer on our MBE system to measure temperatures accurately is around 475°C, results in a small window for potential growth
temperature. For the growth of Ga$_{0.51}$In$_{0.49}$P in this group in the past [9-12], 490°C was used. The requirements for growth temperature of Ga-rich compositions of Ga$_x$In$_{1-x}$P is not expected to change the requirements for low temperature growth, and so was not investigated here. Additionally, previous i-group investigations on the V:III ratio for the growth of Ga$_{0.51}$In$_{0.49}$P found that ratios from 6:1 to 12:1 produced the highest quality films.

The equilibrium lattice constant of Ga$_{0.57}$In$_{0.43}$P is approximately 5.632 Å, about 0.4 % smaller than that of GaAs. This difference is large enough that the direct growth of an epitaxial layer, of thickness larger than its critical thickness, on a (100) substrate with this amount of lattice mismatch is sufficient to create a significant number of threading dislocations. As discussed in Chapter 3, a step-graded buffer is used to create a virtual substrate with a terminal layer of lattice constant nominally equal to that of the epitaxial layer to be grown in order to minimize threading dislocations in the epitaxial layer. MOCVD-grown, n-type GaAs$_{0.90}$P$_{0.10}$ metamorphic tensile-graded buffers grown on (100) GaAs substrates (offcut 6° towards <111>A) were used as virtual substrates for investigations of Ga$_{0.57}$In$_{0.43}$P layers and devices. These step-graded buffers included four layers of GaAs$_y$P$_{1-y}$ with composition changes of 2.5% in each layer, to reach 90% AsGaAsP by the final layer. The structure is shown in Figure 6.1 (a) and the HRXRD-measured reciprocal space map (RSM) is shown in Figure 6.1 (b). Figure 6.1 (c) shows results from an electron beam-induced current (EBIC) image from a solar cell on this buffer. For samples discussed in this chapter, threading dislocations were averaged per area for a number of images, with a total counting area of about 8,300 µm$^2$, resulting in an estimate for threading dislocation densities (TDD) for these GaAs substrate-based virtual substrates of $3.4 \times 10^5$ cm$^{-2}$. 
Figure 6.1: (a) HRXRD-measured reciprocal space map of the glancing incidence (224) reflection, (b) schematic structure of the graded buffer and (c) Plan-view EBIC image of an n⁺p Ga₀.₅₇In₀.₄₃P solar cell grown on the same step-graded buffer showing a dislocation density of 3×10⁵ cm⁻².
Initial testing of the Ga$_{0.57}$In$_{0.43}$P layers included HRXRD measurements to determine exact alloy compositions and layer strains as well as PL and Hall effect measurements to judge material quality. The growth conditions selected (490°C, 9:1 V:III ratio) were found to provide good lattice matching, good PL response, and Hall mobilities in line with those reported for MBE-grown Ga$_{0.51}$In$_{0.49}$P [13], in the range of 580 – 620 cm$^2$/Vs for n-type layers doped with Si at a concentration of 2×10$^{18}$ cm$^{-3}$. All solar cell layers exhibited small strain, less than 0.15.

6.2.1 Anneal

Post-growth anneals, proven effective for Ga$_{0.51}$In$_{0.49}$P solar cells in past studies [9, 10, 14], were used to test for material quality improvements of the Ga$_{0.57}$In$_{0.43}$P layers. Figure 6.2 shows low temperature PL measurements of an n-type Ga$_{0.57}$In$_{0.43}$P sample doped 2×10$^{17}$ cm$^{-3}$. Two clear peaks separated by 32 meV are observed in the PL spectrum of the annealed sample. The higher energy peak most likely results from an emission involving the band-edge due to its high intensity and relatively small line width (FWHM ~ 15 meV). The lower energy peak shows a broader line width (FWHM ~ 34 meV), indicating the spreading of energy levels associated with donor and acceptor transitions. While it is not possible to determine exactly the mechanism causing this radiative recombination from this measurement alone, the energy separation of 32 meV suggests that it could involve compensating acceptor levels which, for Ga$_{0.51}$In$_{0.49}$P, have activation energies of 30 – 60 meV [15-17]. Additionally, the spectrum of the as-grown sample actually seems to show a mixing of multiple peaks and could represent radiative recombination through levels created by crystalline imperfections (expected for materials grown at low temperature) that can be repaired by annealing. In that case, the ratio of the
intensities of the band-edge peak to the secondary peak would be a potential qualitative measure of material quality; as non-radiative recombination causing traps are removed through annealing, the luminescence increasingly originates from band-edge transitions, thereby increasing the intensity of the band-edge peak relative to other emissions, as seen for the annealed PL spectrum. Regardless, the increased emission intensity from the primary peak suggests an improvement in the material. This should have the effect of increasing minority carrier lifetimes which will increase the collection probability of electron-hole pairs generated by photon absorption in a solar cell.

Figure 6.2: Low temperature (20 K) PL of n-type Ga0.57In0.43P comparing emission from an as-grown sample to one receiving a 5 minute, 680°C anneal in the MBE chamber.
6.3 Solar Cells Grown on GaAs

Solar cells were processed by standard lithography techniques. Cr/Au metal stacks were used to make back-side (p-type) ohmic contacts. Top (n-type) ohmic contacts were made with a Ni/GeAu/Ni/Au metal stack, annealed at 400°C; front-side metal grid coverage was 8.4%. Mesa isolation for the cells was realized via dry etching using a SiCl₄/BCl₃ chemistry in an inductively-coupled plasma reactive ion etch system, producing total cell areas of 4 mm².

6.3.1 Anneal

A series of n⁺p Ga₀.₅₇In₀.₄₃P solar cells were grown on p-type MOCVD-grown tensile step-graded buffers as shown in the previous section. The basic structure of these cells is depicted in Figure 6.3. For each cell, the p-type base was doped 5×10¹⁶ cm⁻³ with Be and the n-type emitter was doped 2×10¹⁸ cm⁻³ with Si. Each solar cell sample was cleaved after growth to allow a comparison of as-grown material to annealed material. One of the cleaved pieces was re-mounted and loaded back into the MBE system for a 5 minute anneal at 680°C, as reported in the previous section, and then processed alongside the as-grown portion of the sample to allow direct observation of the effect of the anneal on device performance.
DIV measurements are shown in Figure 6.4 (a). The experiments used a Keithley 2400, and the very low currents of these large bandgap devices at low bias values become too low for accurate measurement by the instrument below about 0.7 V forward bias. A comparison of the DIV curves from the as-grown and annealed samples shows a significantly decreased forward current after annealing. As will be shown (section 6.4.2), the recombination-based reverse saturation current $J_0$ dominates the forward current for these devices until around 1.3 V. This means that the reduction in current observed...
indicates a reduction in the concentration of recombination centers in the Ga\textsubscript{0.57}In\textsubscript{0.43}P material, supporting the conclusions from the PL measurements.

The lighted I-V measurements in Figure 6.4 (b), measured under the one-sun, AM1.5G spectrum as described in Chapter 2, confirm the anneal-related material improvement in that the performance metrics sensitive to depletion region recombination, the \textit{V}\textsubscript{OC} and FF, are significantly improved. The extracted parameters provided in Table 6.1 show significant increases in \textit{V}\textsubscript{OC} (80 meV) and FF (2.6%) and the important role of annealing the solar cell structures. It is important to note here that since the anneal has not yet been optimized for this material (neither anneal temperature nor duration have been varied), further improvements in these metrics are likely.
Figure 6.4: DIV and LIV curves from a Ga$_{0.57}$In$_{0.43}$P solar cell demonstrating the effects of a 5 minute, 680°C anneal in the MBE system.
Table 6.1: Extracted LIV performance parameters from the data of Figure 6.4 (b).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>As Grown</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>V_{oc} (V)</strong></td>
<td>1.26</td>
<td>1.34</td>
</tr>
<tr>
<td><strong>FF</strong></td>
<td>83.8%</td>
<td>86.4%</td>
</tr>
<tr>
<td><strong>J_{SC} (mA/cm^2)</strong></td>
<td>9.34</td>
<td>9.56</td>
</tr>
</tbody>
</table>

Collection probability was also observed to improve over much of the measured spectrum as seen in the EQE curves of Figure 6.5, indicating a reduction in carrier recombination and an increase in carrier lifetime. This effect, however, is limited by the transmission of longer wavelength light through the thin Ga_{0.57}In_{0.43}P absorber layers. This is reflected by the modest increase in J_{SC} (~ 0.2 mA). This effect can also be verified by simple device modeling. Figure 6.6 shows results from a model performed by PC1D, a commonly used 1 dimensional solar cell modeling software [18], mimicking the solar cell structure presented here and structures for which the base thickness is increased while keeping all other parameters fixed. Collection efficiency is observed to increase significantly with increasing base thickness. The effect is strongest for longer wavelengths which have smaller absorption coefficients and are therefore absorbed deeper in the material. This explains why the anneal does not affect the long wavelength QE response in
the experimental data of Figure 6.5. The solar cell is simply not thick enough to absorb those photons. This effect is shown experimentally in Chapters 7, where MOCVD-grown Ga$_{0.57}$In$_{0.43}$P solar cells with thicker bases are grown and processed, and 8, where ongoing work to optimize these MBE-grown solar cells is described.

Figure 6.5: External quantum efficiency curves, adjusted for measured reflection, comparing the response of the as-grown solar cell to that of the sample receiving the 5 minute, 680°C anneal.
6.3.2 Cell structure tests

With the beneficial effects of a post-growth anneal established, additional tests were performed on different window and BSF layers. For the window layers, $\text{Al}_{0.57}\text{In}_{0.43}\text{P}$ was compared to $(\text{Al}_{0.7}\text{Ga}_{0.3})_{0.57}\text{In}_{0.43}\text{P}$ and for the BSF layers, $\text{Ga}_{0.57}\text{In}_{0.43}\text{P}$ was compared to $(\text{Al}_{0.3}\text{Ga}_{0.7})_{0.57}\text{In}_{0.43}\text{P}$. Test samples of these materials were grown to ensure that target compositions and doping levels were accurate. In all the cases, the thickness and doping
levels of the window and BSF layers were kept the same: 30 nm and \(5 \times 10^{18} \text{ cm}^{-3}\) for the windows and 30 nm and \(3 \times 10^{18} \text{ cm}^{-3}\) for the BSFs. These tests were performed on otherwise nominally identical Ga\(_{0.57}\)In\(_{0.43}\)P cells which were grown and fabricated on GaAs substrates using tensile-graded GaAs\(_y\)P\(_{1-y}\) buffers. All structures received the post-growth anneal as just described.

The influence of the choice between Al\(_{0.57}\)In\(_{0.43}\)P and (Al\(_{0.7}\)Ga\(_{0.3}\))\(_{0.58}\)In\(_{0.42}\)P window layers on device properties are demonstrated in Figure 6.7, which shows DIV and LIV results, and Table 6.2, which shows the extracted LIV parameters. The DIV data show negligible influence of substituting the window layer materials on the forward-bias dark diode current, which is reflected in the LIV data where the \(V_{oc}\) is found to be effectively independent of window layer material. The photocurrent, however, is found to show a clear improvement with the Al\(_{0.57}\)In\(_{0.43}\)P window. Such a result should actually be expected for this material due to its larger direct bandgap versus (Al\(_{0.7}\)Ga\(_{0.3}\))\(_{0.57}\)In\(_{0.43}\)P, \(~2.5\) vs. \(~2.3\) eV [19], respectively. The EQE/(1-R) data in Figure 6.8 corroborates this by showing an increased carrier collection efficiency in the shorter wavelength region that would be dominated by collection of photocarriers from the emitter layer of the solar cell. The fact that the \(V_{oc}\) does not degrade is important since this signifies that in spite of the higher Al content for Al\(_{0.57}\)In\(_{0.43}\)P, the quality of the Al\(_{0.57}\)In\(_{0.43}\)P/Ga\(_{0.57}\)In\(_{0.43}\)P in terms of interface recombination velocity appear to be comparable with the lower Al-content quaternary window. Alternatively, it is also possible that the base and base/BSF interface are limiting the \(V_{oc}\) such that window/emitter interfacial issues are effectively swamped. Indeed, the fact that the \(V_{oc}-E_g/q (W_{oc})\) offset is \(~0.6\) V, as opposed to the theoretically ideal value of about 0.4 V, suggests that recombination losses are in fact present, and is the subject of
the following sections. This value is lower than devices of comparable composition grown by CVD [20], but comparable to other MBE grown samples [21] from the literature.

Figure 6.7: (a) Dark current voltage (DIV) measurements (note that for lower voltages the current magnitude was below detection limits and is not shown for clarity), and (b) one sun AM1.5G lighted current voltage (LIV) measurements of Ga_{0.57}In_{0.43}P n’p solar cells grown on GaAs_{y}P_{1-y}/GaAs tensile graded buffers with different window and BSF layers, as indicated in the legend.
Figure 6.7 also shows the influence of changing the BSF layer from \((\text{Al}_{0.3}\text{Ga}_{0.7})_{0.57}\text{In}_{0.43}\text{P}\) to \(\text{Ga}_{0.57}\text{In}_{0.43}\text{P}\) on the same device characteristics. Use of the homojunction BSF greatly reduces the forward bias dark diode current, translating to an increased \(V_{\text{oc}}\) in the LIV, in addition to a slightly increased \(J_{\text{sc}}\). This higher photocurrent is consistent with the quantum efficiency measurement data shown in Figure 6.8, for which a uniform increase in carrier collection is observed. Taken together, these results suggest either an overall degradation in material quality of the active solar cell layers or a higher level of base/BSF interface recombination due to the \((\text{Al}_{0.3}\text{Ga}_{0.7})_{0.58}\text{In}_{0.42}\text{P}\) BSF. This is significant since it means that the transport properties of the bulk base layer become dominated by either a base/BSF interface that is characterized by a large interface recombination velocity or by the sensitivity of the base material quality to growth on the \((\text{Al}_{0.3}\text{Ga}_{0.7})_{0.58}\text{In}_{0.42}\text{P}\) BSF material itself (both of which might be related to incorporation of excess oxygen due to the Al-containing BSF material). Coupled with the strong effect of annealing described above, it is clear that the base and base/BSF material quality for these MBE-grown cells is likely to be the limiting layer in terms of maximizing \(\text{Ga}_{0.57}\text{In}_{0.43}\text{P}\) cell performance for a given structure. Further optimization would be needed to fully capture the theoretical advantages of the larger bandgap quaternary BSF layer based on MBE growth. One possible strategy would be to use a dual-layer \(p^+ \text{Ga}_{0.57}\text{In}_{0.43}\text{P}/p^+ \text{Al}_{0.57}\text{In}_{0.43}\text{P}\) BSF, which has been shown to be effective for MOCVD-grown \(n^+p\ \text{Ga}_{0.51}\text{In}_{0.49}\text{P}\) solar cells [22].
Figure 6.8: External quantum efficiency measurements, adjusted for the measured reflectance (EQE/(1-R)), comparing different window (Al$_{0.57}$In$_{0.43}$P vs. (Al$_{0.5}$Ga$_{0.3}$)$_{0.57}$In$_{0.43}$P) and BSF (Ga$_{0.57}$In$_{0.43}$P and (Al$_{0.3}$Ga$_{0.7}$)$_{0.58}$In$_{0.42}$P) layer materials for n$^+$p Ga$_{0.57}$In$_{0.43}$P single junction solar cells on a GaAs$_y$P$_{1-y}$/GaAs tensile graded buffer.

Table 6.2 summarizes the extracted solar cell LIV parameters for the window and BSF comparison data sets. All results shown are for cells that received post-growth anneals. The results of the past few figures are clearly evident in the tabulation. For the cell thickness and bandgap used here, the theoretical value for $J_{SC}$, removing the effects of surface reflection and front contact grid obscuration from the measured data, is 10.1
mA/cm\(^2\) for the same nominal spectrum, very close to what is measured here, in spite of the residual threading dislocation density of \(3.4 \times 10^5\) cm\(^{-2}\).

Table 6.2: One-sun, room temperature, AM1.5G lighted current-voltage (LIV) measurement parameters of annealed Ga\(_{0.57}\)In\(_{0.43}\)P solar cells grown on GaAs substrates with different window and BSF layers, as indicated.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>GaAs</th>
<th>GaAs</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Window</td>
<td>Al(<em>{0.58})In(</em>{0.42})P</td>
<td>Al(<em>{0.58})In(</em>{0.42})P</td>
<td>(Al(<em>{0.7})Ga(</em>{0.3}))(<em>{0.58})In(</em>{0.42})P</td>
</tr>
<tr>
<td>BSF</td>
<td>(Al(<em>{0.3})Ga(</em>{0.7}))(<em>{0.58})In(</em>{0.42})P</td>
<td>Ga(<em>{0.57})In(</em>{0.43})P</td>
<td>Ga(<em>{0.57})In(</em>{0.43})P</td>
</tr>
<tr>
<td>(V_{OC}(V))</td>
<td>1.30</td>
<td>1.34</td>
<td>1.32</td>
</tr>
<tr>
<td>(J_{SC}(\text{mA/cm}^2))</td>
<td>9.16</td>
<td>9.56</td>
<td>8.83</td>
</tr>
<tr>
<td>FF (%)</td>
<td>84.1</td>
<td>86.4</td>
<td>86.1</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>10.0</td>
<td>11.1</td>
<td>10.1</td>
</tr>
</tbody>
</table>

6.4 Influence of Threading Dislocation Density

Ga\(_{0.57}\)In\(_{0.43}\)P solar cells were grown and fabricated on compressive metamorphic step-graded buffers on GaP and Si substrates to investigate the influence of threading dislocation density (TDD). The compressive buffer grown on GaP used 15 steps of 6% composition change at 225 nm each, resulting in a grading rate of 0.99% misfit/\(\mu m\). The compressive buffer grown on a CVD-grown GaP/Si template used a slightly different buffer design with 18 steps of 5% composition change at 200 nm each, resulting in a grading rate of 0.94% misfit/\(\mu m\). These buffers on GaP and GaP/Si were grown via MBE at 680\(^\circ\)C with a growth rate of 1 \(\mu m/hr\). Structural analysis was provided by HRXRD analysis of the virtual substrates which showed all layers fully relaxed at room temperature and possessing a measurable but negligible residual strain. Reciprocal space maps are
shown in Figure 6.9 and Figure 6.10, which show evenly spaced composition changes throughout the graded buffer structures. Nomarski micrographs are also presented for both showing the crosshatch present on the surface of the terminal layers of the buffers. The surface is visibly smoother for the GaP-based buffer than for the Si. Threading dislocations are again counted by EBIC measurements of the solar cells subsequently grown on the buffers: $6.7 \times 10^6$ cm$^2$ for GaP, and $4.2 \times 10^7$ cm$^2$ for Si, providing a wide range with which to study the effects of TDD on these high bandgap devices.
Figure 6.9: (a) HRXRD-measured reciprocal space map of the glancing incidence (224) reflection and (b) a Nomarski micrograph of a step-graded metamorphic GaAs$_x$P$_{1-x}$ buffer grown on GaP. (c) Plan-view EBIC image of an n$^+$ p Ga$_{0.56}$In$_{0.44}$P solar cell grown on the same step-graded buffer.
Figure 6.10: (a) HRXRD-measured reciprocal space map of the glancing incidence (224) reflection and (b) a Nomarski micrograph of a step-graded metamorphic GaAs$_y$P$_{1-y}$ buffer grown on Si. (c) Plan-view EBIC image of an n+p Ga$_{0.56}$In$_{0.44}$P solar cell grown on the same step-graded buffer.
The basic solar cell device design used in this section, including material compositions, layer thicknesses, doping levels, and n-on-p polarity, was unchanged throughout the experiment, and is diagramed in Figure 6.11. The design is identical to one of those grown on a tensile-graded buffer from the previous section: Ga$_{0.57}$In$_{0.43}$P back surface field layers and (Al$_{0.7}$Ga$_{0.3}$)$_{0.58}$In$_{0.42}$P window layers were used. Since this work was occurring concurrently with that of the previous section, it had not yet been determined that the Al$_{0.57}$In$_{0.43}$P window layer was preferred. The only variation in the cell structures was virtual substrate and the associated TDD. However, due to wafer availability, in the case of GaP, and band alignment, in the case of Si, the cells grown on these substrates required highly-doped lateral conduction layers (LCLs) to make back-side contact. For ease of reference in the remaining discussion of these samples, they are assigned as sample A, B, and C, indicating the samples grown on GaAs, GaP, and Si substrates, respectively.
6.4.1 LIV Performance

The performance of the solar cells tested on the three different graded buffer-substrate combinations are shown in the LIV curves of Figure 6.12, with the extracted parameters shown in Table 6.3. These results clearly show the well-known behavior of increased $V_{oc}$ accompanying a reduction in density of threading dislocations.
Figure 6.12: One sun AMG1.5 lighted current-voltage measurements of single-junction Ga$_{0.57}$In$_{0.43}$P solar cells grown on buffers of varying TDD.

Table 6.3: Parameters extracted from LIV curves of Ga$_{0.57}$In$_{0.43}$P solar cells grown on Si, GaP, and GaAs substrates using GaAs$_{1-y}$P$_{y}$ metamorphic step-graded buffers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDD (cm$^2$)</td>
<td>3.4×10$^5$</td>
<td>6.7×10$^6$</td>
<td>4.5×10$^7$</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>1.94</td>
<td>1.94</td>
<td>1.95</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>1.32</td>
<td>1.20</td>
<td>1.15</td>
</tr>
<tr>
<td>$J_{sc}$ (mA/cm$^2$)</td>
<td>8.79</td>
<td>8.60</td>
<td>8.56</td>
</tr>
<tr>
<td>FF (%)</td>
<td>87.1</td>
<td>84.8</td>
<td>81.3</td>
</tr>
</tbody>
</table>
Along with \( V_{oc} \), FF is enhanced significantly as TDD is reduced. The FF values provided in Table I have been adjusted to account for the increased series resistance in samples B and C due to the necessary use of lateral conduction layers to make back-side contact. Calculations based on the extracted series resistance from the dark current-voltage curves discussed in the following subsection show a \( R_s \)-related reduction in FF of 2.0 and 2.5% on the solar cells grown on GaP and Si substrates, respectively. Even without the contribution from \( R_s \), a significant increase in FF results from the change in recombination current affecting the sharpness of the Ga\(_{0.57}\)In\(_{0.43}\)P diode turn-on around the maximum power point.

The variation in short circuit current is much less significant. This is not surprising due to the cell structure whose thin base (0.5 \( \mu \)m) provides a relatively wide depletion region due to the low doping (~0.25 \( \mu \)m by calculation), therefore comprising the majority of the base layer and resulting in a short distance that minority carrier electrons must diffuse. This is confirmed by the small differences in the collection efficiency seen in the EQE/1-R scans of Figure 6.13. Collection in the base is limited by transmission through the thin cell and the onset of absorption due to the (Al\(_{0.7}\)Ga\(_{0.3}\))\(_{0.57}\)In\(_{0.43}\)P window at about 540 nm is observed, as pointed out in the previous sections. The steady collection efficiency with changing TDD implies that the defect-mediated recombination is not significant enough to reduce the minority electron lifetime in the base to the extent that it affects the cell performance given the 0.5 \( \mu \)m base width.
Figure 6.13: Internal quantum efficiency (IQE) measurements comparing Ga$_{0.57}$In$_{0.43}$P solar cells grown containing different concentrations of threading dislocations.

At this point, a discussion on the $V_{OC}$ values measured for these cells is needed. As discussed in Chapter 2, it is generally held that a high quality solar cell should have a $V_{OC}$ of about 0.4 V. The larger than expected $V_{OC}$ of sample A (and all of the solar cells discussed in this chapter which were grown on the low-TDD GaAs$_{0.90}$P$_{0.10}$/GaAs buffers) can be explained by the following: First, in the case of sample A, we already know that the use of Al$_{0.57}$In$_{0.43}$P instead of the quaternary window, increases the $V_{OC}$ of these devices to 1.34 V. Further optimization of these solar cell structures, including doping levels and layer
thicknesses, are part of an on-going effort, which, as is shown in Chapter 8, has shown a
$V_{OC}$ improvement to 0.58 V. Additionally, optimization of the post-growth anneal is
expected to offer additional $V_{OC}$ increase. Finally, as has been shown in the past, the larger
mobility of electrons in III-V materials as compared to holes leads to a greater sensitivity
of $V_{OC}$ to TDD for n$^+$p configuration solar cells than for p$^+$n [23]. Simple modeling based
on the method of Ref. [23] (in turn based on the equations presented in Chapter 2) for
Ga$_{0.57}$In$_{0.43}$P-based devices suggest that a $3 \times 10^5$ cm$^{-2}$ density of threading dislocations
already reduces the $V_{OC}$ by about 40 mV.

Another important consideration for Ga$_x$In$_{1-x}$P is composition modulation (CM). As
discussed in Chapter 3, CM can be driven by strain [24] and surface undulations [25] and
the presence of CM-related defects have been shown to be detrimental to optical quality
[26]. While strain should not be an issue for the samples reported here as the solar cell
layers are nominally strain-free, surface undulations are present due to the crosshatch
pattern common to metamorphic layers [27], meaning that the presence of some CM is
possible. In Chapter 8, the ongoing work to characterize this material with transmission
electron microscopy, which can provide evidence for or against the presence of CM, is
presented.

### 6.4.2 Transport and defect measurements

Dark current-voltage measurements were used to test for trends in the behavior of
the diffusion and recombination current component contributions as a function of TDD as
well as to estimate series and shunt resistance values. The data shown in Figure 6.14 were
measured with a Keithley 6514 electrometer and tabulated values of the fitting following
Equation 4.4 are given in Table 6.4. The increased series resistance for samples B and C
are due to the nature of the structure required (LCLs for back-side contact), not to any change in the materials themselves. Shunt resistance is observed to increase with increasing density of threading dislocations, but does not become detrimental to the solar cell performance.

The plotted data of Figure 6.14 reveal significant differences in behavior. For samples B and C, the recombination component of the current dominates the entire forward biased current-voltage characteristic before series resistance effects take over. For the sample with largest TDD, sample C, a unique $J_{01}$ value could not be extracted from the data. This contrasts with the curve for sample A, where at voltages of around 1.3, close to the $V_{OC}$ of the cell, the $J_{01}$ diffusion current begins to influence the dark current noticeably, as indicated by the increased slope. The parameters reflect this overall change in current contribution over the three devices as the $J_{02}$ values tracks fairly well with TDD. The change in ideality factor related to recombination current, $n_2$, also increases with TDD, but is difficult to interpret, especially when multiple levels are involved in the recombination process, as will be shown in the DLOS/DLTS experiments in the next section. From DIV modeling, a quantitative picture of the mitigated dominance of recombination current over diffusion current with TDD reduction is provided. However, in order to be useful for future characterization and to aid in drawing conclusions about material properties, more precise information is required. To more explicitly explore the behavior of defects in these Ga$_{0.57}$In$_{0.43}$P solar cell structures, and to tie the values extracted from this DIV curve analysis to more specific material characteristics, DLTS and DLOS measurements were carried out.
Figure 6.14: Dark current-voltage curves measurements of single-junction, 4 mm² Ga₀.₅₇In₀.₄₃P solar cells grown on metamorphic graded buffers of varying TDD.
Table 6.4: Parameters extracted from DIV curves of Ga$_{0.57}$In$_{0.43}$P solar cells grown on Si, GaP, and GaAs. All measurements are at 300K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDD (cm$^{-2}$)</td>
<td>$3.4 \times 10^5$</td>
<td>$6.7 \times 10^6$</td>
<td>$4.2 \times 10^7$</td>
</tr>
<tr>
<td>$n_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$J_{01}$ (A/cm$^2$)</td>
<td>$9.32 \times 10^{-26}$</td>
<td>$6.25 \times 10^{-25}$</td>
<td>--</td>
</tr>
<tr>
<td>$n_2$</td>
<td>1.70</td>
<td>1.83</td>
<td>1.99</td>
</tr>
<tr>
<td>$J_{02}$ (A/cm$^2$)</td>
<td>$1.86 \times 10^{-16}$</td>
<td>$9.60 \times 10^{-15}$</td>
<td>$8.56 \times 10^{-14}$</td>
</tr>
<tr>
<td>$R_S$ ($\Omega \cdot $cm$^2$)</td>
<td>0.21</td>
<td>4.43</td>
<td>5.33</td>
</tr>
<tr>
<td>$R_P$ ($\Omega \cdot $cm$^2$)</td>
<td>$1.11 \times 10^{11}$</td>
<td>$4.81 \times 10^{10}$</td>
<td>$1.65 \times 10^{10}$</td>
</tr>
</tbody>
</table>

6.4.3 Deep Level Spectroscopy Measurements

DLTS measurements were performed on 0.25 mm$^2$ test diodes processed on the same wafers as the n$^+$ p Ga$_{0.57}$In$_{0.43}$P solar cell structures. The n$^+$ p configuration results in a depletion region lying essentially entirely in the p-type region of the Ga$_{0.57}$In$_{0.43}$P, so that spectroscopy measurements reported here are with respect to p-type Ga$_{0.57}$In$_{0.43}$P. Measurements were made using a quiescent reverse bias of -0.5 V. A 10 ms filling pulse to 0 V was used to fill traps in the p-type base with holes. The temperature range for these measurements was 100-350 K.

The spectra are shown in Figure 6.15 along with plots of the associated Arrhenius analyses whose data is listed in Table 6.5. The spectra are quite similar, with one single majority carrier hole trap detected in all three samples with energy of $E_a = 0.70$ eV above the valence band showing no apparent sensitivity to the number of threading dislocations present in the material. This result agrees well with previous studies on Ga$_{0.51}$In$_{0.49}$P in
which n+p solar cells grown on GaAs and SiGe/Si substrates were compared with DLTS measurements [12]. The results presented here show that even at this significantly different composition, the single ~0.7 eV trap concentration persists with the same activation energy relative to the valence band. It also provides further evidence for the conclusions of reference [12] that this trap is native to the Ga_{x}In_{1-x}P material system.
Figure 6.15: (a) DLTS spectra obtained for Ga$_{0.57}$In$_{0.43}$P n$^+$p solar cells grown on virtual substrates with varying TDD. The data shown corresponds to a measurement rate window of 0.8 s$^{-1}$. (b) DLTS data for a range of rate windows is shown in the usual Arrhenius format from which the activation energy and capture cross section are derived. These values are listed in Table III.
Table 6.5: Numerical results of DLTS analysis for the primary DLTS trap at Ec - 0.7 eV as function of TDD for p-type Ga\textsubscript{0.57}In\textsubscript{0.43}P layers grown by MBE.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDD (cm\textsuperscript{-2})</td>
<td>3.4×10\textsuperscript{5}</td>
<td>6.7×10\textsuperscript{6}</td>
<td>4.2×10\textsuperscript{7}</td>
</tr>
<tr>
<td>Activation Energy (eV)</td>
<td>EV + 0.69</td>
<td>EV + 0.72</td>
<td>EV + 0.72</td>
</tr>
<tr>
<td>Cross Section (cm\textsuperscript{2})</td>
<td>3.53×10\textsuperscript{-15}</td>
<td>2.73×10\textsuperscript{-14}</td>
<td>2.40×10\textsuperscript{-14}</td>
</tr>
<tr>
<td>Concentration (cm\textsuperscript{-3})</td>
<td>1.41×10\textsuperscript{13}</td>
<td>1.96×10\textsuperscript{13}</td>
<td>1.48×10\textsuperscript{13}</td>
</tr>
</tbody>
</table>

In order to observe states deeper in the bandgap than ~1.0 eV (the approximate limit of DLTS measurements), steady state photocapacitance measurements were performed. The measurements were performed at 300 K and used a -2 V quiescent reverse bias with a trap filling pulse of 0 V for 10 ms followed by a settling time of 30 s in the dark prior to optical excitation as a function of wavelength. The purpose of the settling time is to allow “faster” thermal emission transients from shallow traps to die out so that changes in capacitance are known to be from photoexcitation. This is why the defects measured by DLTS are not present in these spectra. The 4 mm\textsuperscript{2} solar cells themselves were used. Measurements for samples B and C, which used lateral conduction layers, were found to give spurious results due to nature of the GaAs\textsubscript{0.90}P\textsubscript{0.10} lateral conduction layer and back ohmic contact set up. Light incident on the sample is directly incident on the LCL due to the mesa definition, and the fact that the back ohmic contact is actually on the front of the sample means that photocarriers in the GaAs\textsubscript{0.90}P\textsubscript{0.10} LCL can diffuse to the contact and affect the capacitance. This resulted in extra capacitance onsets around the bandgap of
GaAs$_{0.90}$P$_{0.10}$, ~1.55 eV. This is proven by sample A, whose back contact is formed on the actual back side of the wafer, which did not exhibit any onsets in the region of 1.55 eV. For samples B and C, a shadow mask was used to cover the entire area of the sample except for the solar cell to be measured and a portion of the ohmic contact.

Figure 6.16: Steady state photocapacitance spectra obtained at 300 K for 1.95 eV bandgap, p-Ga$_{0.57}$In$_{0.43}$P grown on different virtual substrates. Several deep levels are indicated with positive onsets referring to the valence band.

The steady state photocapacitance (SSPC) results plotted in Figure 6.16 reveal two additional bandgap states. Here, positive onsets in the photocapacitance indicate carrier
(hole) emission from a deep level to the majority carrier band, in this case the valence band. All three samples exhibit positive onsets at 0.90 eV and 1.82 eV above the valence band, indicating the presence of majority hole traps at those energies. Estimations for trap concentrations taken from SSPC spectra can only be minimum value estimates, which are listed in Table 6.6. Nonetheless, samples B and C show clear, significant increases in the concentration of $E_V + 0.90$ eV. This suggests that the level closest to the midgap and therefore likely the most efficient recombination center is enhanced by TDD. Examination of the capacitance transients (DLOS) and fitting of these profiles are still required to determine the optical capture cross-section and more precise estimations of activation energy.

Table 6.6: Minimum estimates for the concentration of traps observed in SSPC measurements for the p-type $\text{Ga}_{0.57}\text{In}_{0.43}\text{P}$ base layers of the solar cells grown on virtual buffers of varying TDD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDD (cm$^{-2}$)</td>
<td>3.4×10$^5$</td>
<td>6.7×10$^6$</td>
<td>4.2×10$^7$</td>
</tr>
<tr>
<td>$E_V + 0.90$ eV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration (cm$^{-3}$)</td>
<td>4.7×10$^{13}$</td>
<td>6.8×10$^{13}$</td>
<td>1.2×10$^{14}$</td>
</tr>
<tr>
<td>$E_V + 1.82$ eV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Concentration (cm$^{-3}$)</td>
<td>3.9×10$^{13}$</td>
<td>6.2×10$^{13}$</td>
<td>5.2×10$^{13}$</td>
</tr>
</tbody>
</table>
6.5 Summary

The work described in this chapter to optimize the top junction subcell represents a step toward the realization of III-V multijunction solar cells integrated with Si. The material properties, transport properties, solar cell performance and distribution of deep levels have been discussed. Building on the knowledge gained through several decades of research on lattice matched Ga\textsubscript{0.51}In\textsubscript{0.49}P, the findings reported here extend the understanding of this ternary alloy into new compositions integrated with different
substrates. The information gained in this work will aid the fabrication and improvement of Ga-rich, high bandgap Ga\textsubscript{x}In\textsubscript{1-x}P, whose place in the photovoltaic field at large will be indispensable since high bandgap top junctions are a major goal for many avenues of III-V PV research. More information on the on-going efforts, including TEM and continued cell optimization, is given in Chapter 8 of this dissertation.

6.6 References


Chapter 7

Growth and Characterization of
Ga$_{0.57}$In$_{0.43}$P Solar Cells Grown by MOCVD

7.1 Introduction

Another path undertaken to explore the performance and development of high bandgap Ga$_{x}$In$_{1-x}$P solar cells is the investigation of subcells created using the MOCVD growth environment, parallel to the MBE-based study. MOCVD growth of Ga$_{x}$In$_{1-x}$P affords several advantages over the MBE environment, most notably higher growth temperature, larger possible V:III ratio and faster growth rates allowing a much greater degree of freedom for optimizing material quality. While both MOCVD and MBE are capable of creating extremely high quality, high efficiency solar cells [1-3], MOCVD offers the particular advantage that the growth of Ga$_{x}$In$_{1-x}$P is not limited to the same low-temperature regime as in MBE. Furthermore, comparison of material grown by the two techniques provides a unique research opportunity to understand in greater depth the differences between the epitaxial materials created by each.
7.2 \textbf{Ga}_{0.57}\textbf{In}_{0.43}\textbf{P CVD Growth Conditions}

As discussed in Chapter 3, \textit{Ga}_{0.51}\textit{In}_{0.49}\textit{P} grown by MOCVD has been studied extensively and so there is a significant number of reports regarding growth conditions. High quality devices are generally grown at high temperatures, greater than or equal to 700°C [4-6]. Two important implications of the growth conditions of \textit{Ga}_x\textit{In}_{1-x}\textit{P}, which were discussed in Chapter 3 and bear repeating briefly here, are the effects of CuPt\textsubscript{B} ordering and composition modulation. CuPt\textsubscript{B} ordering results in a U-shaped trend for the bandgap of \textit{Ga}_{0.51}\textit{In}_{0.49}\textit{P} with respect to growth temperature, where for medium range temperatures the degree of ordering, and therefore bandgap reduction, is greatest [7]. High temperature growth results in adatoms with higher thermal energy that randomize the crystal and avoid ordering thereby providing the largest bandgap. Given a high growth temperature, large V:III ratios have been used to suppress composition modulation which have been found to be detrimental to optical material quality [8].

7.2.1 \textbf{Characterization by HRXRD and PL}

Three \textit{Ga}_{0.57}\textit{In}_{0.43}\textit{P} test samples were grown at growth temperatures of 625°C, 650°C and 675°C and with a V:III flow rate ratio of 261:1. The same nominal tensile-graded buffers on GaAs as those used for the MBE-based study were used here. The samples were tested by HRXRD and PL to confirm composition and bandgap.

Reciprocal space maps from HRXRD measurements are shown in Figure 7.1. The layer grown at 625°C shows the diffraction peak from a \textit{Ga}_x\textit{In}_{1-x}\textit{P} layer of $x = 57.3\%$, slightly mismatched from the terminal layer of the GaAs\textsubscript{y}P\textsubscript{1-y} buffer ($y = 89.5\%$) for this particular growth run. This mismatch results in a small amount of lattice strain, 0.065. As
the growth temperature is increased, the diffraction peak appears to split into separate peaks despite the fact that the same composition was targeted for each sample, using the same precursor flow rates. At 650°C, an additional diffraction peak is observed despite using the same virtual substrate and growth recipe. Two diffraction peaks even further separated are evident in the 675°C sample, with a 2% difference in relative Ga composition and the Ga-poor diffraction peak actually coinciding with the terminal buffer layer.

This phenomenon is believed to be the result of severe composition modulation in the layer in which the alloy is separated into distinct phases of different composition. This would be a surprising result, given that the strain resultant from the slight mismatch of the epitaxial layer is only 0.065. For comparison, a study concerning Ga$_x$In$_{1-x}$P samples grown on GaAs substrates by MBE reported no signs of composition modulation for a strain level of 0.18 [9], although these samples were grown under much different conditions. It is possible that the composition modulation is driven by a number of factors such as the strain resulting from the slight lattice mismatch of the layer, the surface undulations resultant from the cross-hatch pattern of the graded buffer, and the increasing growth temperature, which have provided the surface adatoms with enough bias and energy to separate into Ga-rich and In-rich regions. An important caveat to this is that changing growth conditions in the MOCVD system can also change the cracking efficiency of the precursor molecules at the growth surface, meaning that the actual proportions of constituent atoms available may change. While 50°C is not a huge difference, it is possible that the lattice mismatch of the target layer, and therefore the magnitude of strain, may have shifted.
Figure 7.1: (a) 004 reciprocal space maps measured for n-Ga$_{0.57}$In$_{0.43}$P layers grown on GaAs$_y$P$_{1-y}$/GaAs tensile graded metamorphic buffers by MOCVD with only growth temperature varied - 625°C, 650°C, and 675°C. GaAs substrate and step-graded buffer are diffraction peaks are labeled. Ga$_x$In$_{1-x}$P layers are marked by tie-lines indicating the separation of the diffraction peak with increased growth Temperature. (b) Composition (X = % Ga) and strain of the measured Ga$_x$In$_{1-x}$P layers in the three samples.
Low temperature photoluminescence measurements seem to support this initial conclusion. Figure 7.2 shows the low temperature (21K) photoluminescence emission spectra for these three samples. Emission from the Ga$_x$In$_{1-x}$P layers are from 2.01 – 2.04 eV. Emission from the GaAs$_y$P$_{1-y}$ buffer layers are also observed at around 1.6 eV. Figure 7.2 reveals an increasing FWHM for the Ga$_x$In$_{1-x}$P peaks with increasing growth temperature, from 17.2 meV for 650°C to 22.2 meV for 675°C. In the case of the highest growth temperature, the higher bandgap phase evidently dominates the emission with the peak increasing from 2.01 eV to 2.04 eV. Room temperature measurements were also performed on these samples, with the respective emission energies ranging from 1.94 to 1.97 eV. Additionally, the sample grown at 675°C shows a significantly reduced emission from the GaInP layer as well as a large, extremely broad emission centered on 1.4 eV. This seems to suggest a major defect level that could result from the composition modulation and associated strain present making for poorer crystalline quality.

Since microstructure properties such as CuPt ordering and composition modulation in Ga$_x$In$_{1-x}$P grown by CVD are well known to be very sensitive to growth conditions, the development of optimum growth conditions for Ga$_x$In$_{1-x}$P is expected to be an ongoing pursuit. Following these initial results, the growth parameters used for the layer grown at 625°C were deemed an appropriate starting point for carrying out solar cell device tests, despite the fact that most high quality Ga$_x$In$_{1-x}$P solar cells reported in the literature are grown at higher temperatures. Solar cells are, however, are excellent diagnostic tools for material quality investigation, and will allow for good critical comparison in the future.
7.3 MOCVD-grown Ga\(_{0.57}\)In\(_{0.43}\)P Solar Cells

This section describes the progress made thus far on optimizing the single junction Ga\(_{0.57}\)In\(_{0.43}\)P solar cells grown by MOCVD. The general structure of the cells is shown in Figure 7.3 (a) and the particular changes made to the structure with each incremental improvement in the cell are shown in Figure 7.3 (b). The target doping levels of the p-type
base and n-type emitter were $5 \times 10^{16}$ cm$^{-3}$ and $2 \times 10^{18}$ cm$^{-3}$ respectively. The cells will be referred to as Gen1, Gen2, Gen3 and Gen4 for convenience. The quantum efficiency and lighted current-voltage results are shown in Figure 7.4 and Figure 7.5, respectively, and the tabulated LIV parameters are given in Table 7.1.

Figure 7.3: (a) General structure of the MOCVD-grown Ga$_{0.57}$In$_{0.43}$P solar cells. (b) Table indicating the changes made to the BSF layer material, the base thickness, and the emitter doping during the optimization process of these devices.
7.3.1 Optimization: Emitter Doping

The first two cells grown, Gen1 and Gen2, were fabricated side by side. Gen1 was designed to imitate the structure of the best of the MBE-grown cells of Chapter 6, with an Al\textsubscript{0.57}In\textsubscript{0.43}P window and a p\textsuperscript{+}-Ga\textsubscript{0.57}In\textsubscript{0.43}P BSF. Gen2 used a 1.0 µm thick base and a p\textsuperscript{+} Al\textsubscript{0.57}In\textsubscript{0.43}P BSF. While the EQE curves clearly show the benefit of using the thicker base, these two cells were severely limited by a front-side effect, implied by the poor short wavelength response. This sort of effect could be due to a poor window/emitter interface in which a high interface recombination velocity acts as a sink for carriers, killing the collection of any photocarriers that have made it to the front of the solar cell, or a poor quality emitter, in which the probability of minority carriers recombining before arriving at a contact. Several tests were carried out to solve this problem involving test layers mimicking the target composition and doping levels of the window and emitter. It was discovered that the dopant concentration in the emitter was high. C-V measurements revealed a dopant concentration of just over 1×10\textsuperscript{19} cm\textsuperscript{-3} and Hall effect returned 4.5×10\textsuperscript{18} cm\textsuperscript{-3}. A discrepancy in these measurements is typically due to the fact that C-V measurements are sensitive to the total ionized donor concentration while Hall effect measurements concern free carriers. This result indicates a significantly different cracking efficiency of silane in the growth of Ga\textsubscript{x}In\textsubscript{1-x}P than for GaAs and GaAs\textsubscript{0.90}P\textsubscript{0.10}, which were used as doping calibrations grown at 600°C and 650°C, which is the subject of ongoing investigation.
Figure 7.4: Quantum efficiency measurements performed on the MOCVD-grown solar cell structures of Figure 7.3. The best performing MBE-grown solar cell from Chapter 6 is shown for comparison and represented by the dashed line.

Gen3 and Gen4 were grown with emitter doping levels reduced 3 times and 1.7 times, respectively. The result of this change is evident in the quantum efficiency curves which show an enormous improvement over the entire range of wavelengths. The magnitude of this impact shows that the level of Si doping present in the emitter wreaked havoc with the material quality of the layer. As Si is known to occupy group V sites at high enough concentrations, compensating Si acceptor levels were likely present, inducing
recombination in the depletion region. Another test of the emitter doping concentration was performed to determine its true concentration in the Gen3 device. This resulted in a C-V measured concentration of $5.6 \times 10^{18}$ cm$^{-3}$, still larger than the target, and the improvement observed from Gen3 to Gen4, with a further reduction in silane flow, reflects this. The $J_{SC}$ measured for Gen4 exceeds that of the best MBE-grown cell. A slight reduction in $V_{OC}$ was measured from Gen3 to Gen4, likely the result of the lowered emitter doping, but the overall cell performance was much improved, with the aforementioned $J_{SC}$ increase as well as a significant increase in FF, likely the result of the changed BSF, as discussed in the following section.
Figure 7.5: LIV characteristics comparing MOCVD-grown solar cells grown at 625°C.

Table 7.1: One-sun, room temperature, AM1.5G lighted current-voltage (LIV) measurement parameters of Ga$_{0.57}$In$_{0.43}$P solar cells grown on GaAs substrates following the optimization routine depicted in Figure 7.3. The best performing MBE-grown solar cell is included for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gen1</th>
<th>Gen2</th>
<th>Gen3</th>
<th>Gen4</th>
<th>MBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voc(V)</td>
<td>1.39</td>
<td>1.40</td>
<td>1.42</td>
<td>1.41</td>
<td>1.34</td>
</tr>
<tr>
<td>J$_{sc}$ (mA/cm$^2$)</td>
<td>7.06</td>
<td>8.48</td>
<td>9.55</td>
<td>9.98</td>
<td>9.56</td>
</tr>
<tr>
<td>FF (%)</td>
<td>85.4</td>
<td>84.2</td>
<td>82.9</td>
<td>86.5</td>
<td>86.4</td>
</tr>
</tbody>
</table>
7.3.2 Optimization: BSF Layer

Another point of investigation during the optimization process was the BSF layer. Gen2 and Gen3, which used an Al$_{0.57}$In$_{0.43}$P BSF, each had lower fill factors than Gen1 and also displayed a very strong series resistance-like effect on the current just past $V_{OC}$ as seen in the LIV curves of Figure 7.5. A single Al$_{0.57}$In$_{0.43}$P layer was grown to test its properties. Results from Hall effect measurements revealed the p-type carrier concentration to be $1 \times 10^{17}$ cm$^{-3}$, more than an order of magnitude below its target, $3 \times 10^{18}$ cm$^{-3}$. Due to its high bandgap and band offsets with respect to Ga$_x$In$_{1-x}$P (at least as reported for Ga$_{0.51}$In$_{0.49}$P lattice matched to GaAs [10]), this layer still should have provided an effective blocking layer for minority carriers and as such the long wavelength response for Gen3 was good. The effect of the low doping, however, would be to ensure that a significant portion of the band offset would reside in the majority carrier valence band, thus blocking majority carrier flow in the device. It appears that at some forward bias, just past $V_{OC}$, this effect dominates the transport in the device.

For Gen4, along with the continued decrease in emitter doping, the BSF was switched back to a homo-junction Ga$_{0.57}$In$_{0.43}$P layer. The fill factor for Gen4 is the best of all cells measured, including the MBE cells of the previous chapter. Removing the low doped, resistive Al$_{0.57}$In$_{0.43}$P layer most likely results in a lower series resistance and a better quality diode.

The inability to highly dope Al$_{0.57}$In$_{0.43}$P with Zn in the MOCVD system is actually a well-known issue, with its origins in the LED field since these high bandgap materials were of interest to achieve different wavelengths of visible emission [11]. There are several issues with dimethyl zinc (DMZn) as a p-type dopant for Al$_x$In$_{1-x}$P [11]. First, as the Al
content is increased, the ionization energy of the Zn acceptors increases, reducing the concentration of free carriers at room temperature. Second, higher compositions of Al incorporate higher concentrations of oxygen, which act as compensating deep levels. Finally, DMZn is volatile and requires a very high partial pressure to achieve high doping, which can lead to material quality problems. This was observed in this work when an attempt to increase the doping of the Al$_{0.57}$In$_{0.43}$P layers by increasing the Zn flow resulted in visibly non-specular samples. This also may explain why, for samples Gen2 and Gen3, large defects were observed on the surface of the samples, as shown in the Nomarski microscope image of Figure 7.6. Cells using the homo-junction BSF displayed no such defects, even though an n$^+$-Al$_{0.57}$In$_{0.43}$P was still used for the window layer.
Figure 7.6: Nomarski microscope image of a 4 mm$^2$ solar cell from sample Gen3, which used an Al$_{0.57}$In$_{0.43}$P back surface field, showing surface defects visible as small black dots believed to be the result of high DMZn flows.

Just as for the MBE-grown cells, more investigation is needed to fully exploit the potential benefits of large bandgap, Al-containing BSF layers. In contrast to the MBE-grown samples, the difficulty in achieving highly doped p-type Al$_{0.57}$In$_{0.43}$P precludes it from consideration. Lower Al-content quaternary compounds should allow for higher p-type doping, while providing sufficient carrier blocking in the conduction band.
7.4   Summary

The MOCVD-grown Ga$_{0.57}$In$_{0.43}$P solar cells have thus far shown great promise. The primary deficiency is the $V_{OC}$, which gives a $W_{OC}$ of approximately 0.52 V. Further characterization of the devices presented here, including DIV and DLTS/DLOS, should aid in determining the limiting components. As mentioned earlier, there remains a large space of growth conditions to explore, and so improvements in material quality, and therefore minority carrier lifetime, may be possible.

The continued characterization of these devices affords a fascinating opportunity to study the differences between photovoltaic devices created by MBE and MOCVD. Material quality appears to be better in the MOCVD samples thus far, as interpreted by the larger $V_{OC}$, which could come from a longer minority carrier lifetime. Other aspects of the cells, such as interface quality, deep levels, and microstructural properties, are all also of interest and are worth more investigation. Because solar cells are themselves such a good diagnostic tool for material properties, the scope of this research expands beyond the photovoltaic field.

7.5   References


GaInP/GaAs/GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency, "


Chapter 8

Summary, ongoing and future work

8.1 Summary of this work

The results presented in this dissertation represent steps made toward achieving a high efficiency III-V multijunction solar cell integrated with Si. The work focused on two aspects of such a device: (1) the growth and characterization of GaP, the critical epitaxial component allowing the integration of III-V materials with Si and; (2) the top-junction subcell, whose high bandgap and high quality requirements are satisfied by novel, Ga-rich compositions of Ga_xIn_{1-x}P. In both cases, the growth of these high bandgap phosphides was carried out by both MBE and MOCVD in order to understand the growth behaviors and properties of these materials by these different growth techniques.

In the case of GaP, whose utilization and research drive faded with the advent of high quality heterojunction technologies and the modern epitaxial techniques of MOCVD and MBE in the 1980’s, this dissertation describes comprehensive efforts taken to study films grown by those very methods for the first time. Atomically smooth surfaces resultant from a step-flow growth mode were found for unusually high growth temperatures by MBE. Growth of GaP under similar conditions and temperatures, which are more standard for MOCVD, show very similar surface morphologies. This resulted in identification of a cross-over point in the GaP epitaxial growth phase diagrams for MBE and MOCVD. This represents the first report of step-flow growth of GaP in MOCVD and MBE, which are
expected to aid in the advancement of low-TDD GaAs$_y$P$_{1-y}$ step-graded buffers. Most significant is that this has demonstrated a transition point that connects the worlds of MBE and MOCVD, linking research to production for any future semiconductor device technology that can utilize the GaP/Si heterojunction system.

The electrical properties of the films grown by MBE were found to be similar to those of the old growth techniques, with mobilities on par with material grown by vapor and liquid-phase epitaxial techniques and a similar activation energy for Si donor dopants. DLTS revealed low concentrations of several deep levels, with the most prominent being a level similar to the prominent state found in vapor-phase epitaxy, where it has been suggested to be a defect involving phosphorous vacancies and Si impurities [1], which could well be the case for the intentionally Si-doped GaP layers of Chapter 5.

Ga$_{0.57}$In$_{0.43}$P, with a bandgap of 1.95 eV, was investigated as a top junction subcell for inclusion in an ideal 1.95 eV/1.55 eV/1.12 eV GaInP/GaAsP/Si 3 junction solar cell. Post-growth annealing of the samples was found to be critical to performance, and the combination of an Al$_{0.57}$In$_{0.43}$P window layer and a Ga$_{0.57}$In$_{0.43}$P homojunction BSF was found to exhibit the best performance of the structures tested. Lowering the Al-content of the window only increases the window layer absorption without providing a noticeable improvement from any reduction in window-emitter interface recombination current. Use of a quaternary BSF with Al content of 30% relative to Ga resulted in weaker QE response over the entire span of wavelengths and a lower V$_{OC}$, indicating either an enhanced base-BSF interface recombination velocity or a sensitivity of the material quality of layers grown above the Al-containing BSF, or both.
The effect of TDD on the subcells was studied, with $V_{OC}$ and FF showing sensitivity to the density of threading dislocations. $J_{SC}$ was essentially unaffected for these thin-base structures. DLTS revealed only a single majority carrier trap at $E_V + 0.70$ eV with no sensitivity to the density of threading dislocations, closely following similar work on p-type Ga$_{0.51}$In$_{0.49}$P grown on GaAs substrates and SiGe graded buffers. Steady state photocapacitance measurements revealed two additional levels with activation energies estimated at 0.90 eV and 1.82 eV, also similar to the SSPC spectrum measured in Ref. [2]. Further analysis and curve fitting is necessary to determine the characteristic trap parameters: exact activation energy and optical cross-section.

CVD-grown Ga$_{0.57}$In$_{0.43}$P single junction cells provided better performance overall compared with the MBE-grown counterparts. Larger $V_{OC}$s and better quantum efficiency response suggest a superior material quality. Thicker base widths resulted in a better quantum efficiency for long wavelength light. Al$_{0.57}$In$_{0.43}$P BSF layers resulted in increased series resistance and poorer fill factors due to the inability to obtain sufficiently high p-type doping concentrations in Al$_{0.57}$In$_{0.43}$P. The n-type doping behavior for Ga$_{0.57}$In$_{0.43}$P was found to be significantly different from the GaAs and GaAs0.90P0.10 calibrations. The over-doping of the emitter was found to have a serious detrimental effect on the photovoltaic performance of the first generation devices.

Together, these efforts represent progress toward the goal of a high-efficiency III-V/Si device, which has the potential to make a fundamental and significant reduction in cost of high-efficiency terrestrial solar power generation and therefore its incorporation into the energy production of modern society.
8.2 Ongoing and future work

The following section describes the on-going work in the areas of research discussed in this dissertation. The development of all of the components of a three junction Ga$_{0.57}$In$_{0.43}$P/GaAs$_{0.90}$P$_{0.10}$/Si solar cell is a long-term project. As such, the work presented in this dissertation represents ongoing efforts that are continuing today. These efforts include, but are not limited to, further investigations into: (1) the defect nature of GaP, especially comparing MBE to MOCVD-grown samples; (2) the continued optimization of MBE-grown Ga$_{0.57}$In$_{0.43}$P single junction solar cells; (3) the characterization of Ga$_{0.57}$In$_{0.43}$P material properties grown by both growth systems, including TEM to determine presence of ordering and composition modulation, and DLTS/DLOS to compare deep levels. The current status of these efforts is presented in this chapter.

8.2.1 GaP DLTS

Part of the ongoing work in this study is to expand the scope of deep level measurements on GaP films. One aspect of this is to compare DLTS of samples grown by MOCVD and MBE. To this end, a film grown by MOCVD (725°C, 100:1 V:III) was processed in the same manner as described for the MBE-grown sample of Section 5.4 and tested by DLTS. The Si dopant concentration of the layer, as measured by C-V, was 2.5×10$^{16}$ cm$^{-3}$, about three times larger than for the MBE sample. Initially, the DLTS spectra obtained from the MOCVD-grown sample were measured under slightly different conditions from those of the MBE-grown sample described in Chapter 5. The quiescent reverse bias was -0.5 V instead of -2.0 V. In fact, both samples were originally measured at -0.5 V and the comparison of these initial DLTS spectra is shown in Figure 8.1 and the associated data extracted from the Arrhenius analyses are provided in Table 8.1. The results
reveal a very different spectrum of deep levels for the two films, with a much higher overall trap concentration for the MOCVD-grown sample. A deep level lying at $E_C - 0.84$ eV is the dominant level for the GaP grown by MOCVD while not detected for the MBE-grown sample. It should be noted, however, that the spectrum obtained for the MBE-grown sample under these measurement conditions is different from what was reported in Chapter 5.

Figure 8.1. DLTS measurements comparing two n-type GaP films doped with Si grown by MOCVD and MBE measured with a quiescent reverse bias of -0.5 V and a fill pulse of 0.0 V for 10ms. RW 80 s-1.
Table 8.1. Table of activation energy, capture cross-section, and concentration of deep levels in MBE grown $n$-GaP layer

<table>
<thead>
<tr>
<th></th>
<th>MBE</th>
<th></th>
<th></th>
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<tr>
<td>$E_{C-E_T}$ (eV)</td>
<td>0.19</td>
<td>0.25</td>
<td>0.32</td>
<td>0.53</td>
<td>0.64</td>
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<td>$\sigma_n$ (cm$^2$)</td>
<td>$1\times10^{-15}$</td>
<td>$2\times10^{-15}$</td>
<td>$2.2\times10^{-15}$</td>
<td>$4\times10^{-15}$</td>
<td>$4\times10^{-14}$</td>
</tr>
<tr>
<td>$N_T$ (cm$^{-3}$)</td>
<td>$3\times10^{12}$</td>
<td>$2\times10^{13}$</td>
<td>$1\times10^{12}$</td>
<td>$4\times10^{12}$</td>
<td>$3\times10^{12}$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
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<th></th>
<th></th>
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<th></th>
</tr>
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<tbody>
<tr>
<td>$E_{C-E_T}$ (eV)</td>
<td>0.21</td>
<td>0.32</td>
<td>0.64</td>
<td>0.84</td>
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<td>$\sigma_n$ (cm$^2$)</td>
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<td>$2\times10^{-13}$</td>
</tr>
<tr>
<td>$N_T$ (cm$^{-3}$)</td>
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<td>$2\times10^{13}$</td>
<td>$3\times10^{14}$</td>
<td>$1\times10^{14}$</td>
</tr>
</tbody>
</table>

In addition to the comparison of GaP films grown by MBE and MOCVD, there is also motivation to carry out dedicated efforts to characterize the electronic properties of GaP films grown on Si to complement the structural characterizations already underway including TEM and AFM [3, 4], and electron channeling contrast imaging (ECCI) [5]. Understanding the ways in which GaP films respond to threading dislocations is important both to the entire scope of developing III-V materials on Si as well as to improve the understanding of the ternary compounds $Ga_xIn_{1-x}P$ and $GaAs_{y}P_{1-y}$, for which GaP is the lesser studied of the respective binary endpoints.

**8.2.2 $Ga_{0.57}In_{0.43}P$ by MBE**

The optimization of the MBE-grown $Ga_{0.57}In_{0.43}P$ single junction solar cells is a continuing effort. The most recent cell grown used a base width extended to 1.0 µm and
the base p-type dopant concentration increased to \(1 \times 10^{17} \text{ cm}^{-3}\). The growth missed the target composition slightly, exhibiting a bandgap of about 2.0 eV, as estimated from the absorption edge of the quantum efficiency data of Figure 8.2. Despite the lattice mismatch, the cell performs reasonably well. The \(V_{OC}\) increased as compared to the best cell reported in Chapter 6 to 1.39 V, as shown in the LIV curves of Figure 8.4. Some of this increase is partly due to the increased bandgap, and a complete characterization, including HRXRD and PL to determine the exact composition and bandgap of the cell, is currently underway. Regardless of the true \(V_{OC}\), the base collection is observed to improve, as expected from the increased base width, agreeing with the expectations of Chapter 6. This is a positive result also in light of the increased base doping; there no indication of a detrimental effect on the minority diffusion length.
Figure 8.2: EQE/1-R data comparing the latest generation MBE-grown Ga$_{0.57}$In$_{0.43}$P solar cell to the best performing one of Chapter 6.
Along with optimization of the design of the Ga$_{0.57}$In$_{0.43}$P subcells, there is also space to explore the annealing parameters. Since no attempts have yet been made to optimize the annealing time or temperature, improvements in cell performance can be expected.

Another important and interesting avenue for characterization of the Ga$_{0.57}$In$_{0.43}$P materials grown in this lab is the use of transmission electron microscopy (TEM), which is
generally used to determine the presence of CuPtB ordering and composition modulation. Initial measurements have been carried out and are shown in Figure 8.4, where a [220] dark field cross-sectional TEM (XTEM) image of a Ga_{0.57}In_{0.43}P solar cell is shown. These are the conditions generally used to detect the presence of composition modulation [6-8]. In Figure 8.4 (b), the [110] transmission electron diffraction pattern is given where the presence of CuPtB ordering is observed by the presence of extra, “superspots” between the expected diffraction spots of known patterns [7-9]. The results show no indication of ordering or composition modulation in the Ga_{0.57}In_{0.43}P layers. Ordering was not expected due to the fact that bandgap value measured is close to that expected for completely disordered material [9].
Figure 8.4: (a) $g = [220]$ dark field cross-sectional TEM image of a Ga$_{0.57}$In$_{0.43}$P solar cell grown by MBE with epitaxial layers indicated. (b) [110] transmission electron diffraction pattern showing no sign of CuPt$_{B}$ ordering.
8.2.3 Ga\textsubscript{0.57}In\textsubscript{0.43}P by MOCVD

Ongoing efforts regarding Ga\textsubscript{0.57}In\textsubscript{0.43}P subcells grown by MOCVD include development of a larger bandgap, quarternary BSF layer in order to further improve photocarrier collection. One such layer \(((\text{Al}_{0.15}\text{Ga}_{0.85})_{0.57}\text{In}_{0.43})\text{P})\) has been grown and tested by Hall effect, yielding a bandgap of 2.18 eV and p-type dopant concentration of \(1\times10^{18}\text{ cm}^{-3}\), an order of magnitude higher than the dopant concentration achieved for Al\textsubscript{0.57}In\textsubscript{0.43}P. Achievement of a very high performance structure on GaAs substrates is desired so that as the devices are transferred to GaAs\textsubscript{y}P\textsubscript{1-y} layers grown on Si substrates, there are no doubts about the design of the cell, and any performance degradation can be attributed to threading dislocations. Work toward lowering the threading dislocation density of graded buffers on Si, while not directly a part of this work, is an important goal for the project at large.

While the collection efficiency of the MOCVD-grown subcells are already very good, the \(V_{OC}\) is a parameter that requires improvement. DIV analysis of the devices already presented can be used to obtain evidence for the limiting factors on \(V_{OC}\). Additionally, it may be necessary to return to a study of the growth conditions to improve material quality. As stated in the preceding chapters, Ga\textsubscript{0.57}In\textsubscript{0.43}P grown by MOCVD is generally grown at higher temperatures than those in this work. Due to the limited scope of the growth conditions already studied, it is likely that a better set exists.

Finally, defect spectroscopy of the MOCVD-grown Ga\textsubscript{0.57}In\textsubscript{0.43}P offers a unique opportunity to compare the deep levels of this material to those of the MBE-grown samples. Due to the distinctly different nature of the growth in each system, the relative concentrations of deep levels, and even their presence, can give clues to the nature and
formation of the levels and also provide valuable information for the future development of these types of devices.

Generally speaking, for Ga\textsubscript{0.57}In\textsubscript{0.43}P subcells grown by both growth methods, there are multiple goals beyond the overall efficiency improvements. One is the integration of these devices with compressive buffers grown on Si while maintaining good collection and good \(V_{OC}\) (i.e., maintaining a long minority carrier lifetime). Another is the combination of these cells with other junctions to create multijunction solar cells. The Ga\textsubscript{0.57}In\textsubscript{0.43}P/GaAs\textsubscript{0.90}P\textsubscript{0.10} dual junction on GaAs offers a good opportunity to study the combination of these two junctions which involves current matching considerations and the creation of tunnel junctions.

8.3 References


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