Optimization and Characterization of Indium Arsenide Quantum Dots for Application in III-V Material Solar Cells

Adam M. Podell

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Optimization and Characterization of Indium Arsenide Quantum Dots for Application in III-V Material Solar Cells

by

Adam M. Podell

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Materials Science & Engineering

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Dedication

To my father, Aron Podell, for his support and for being an inspiration throughout.
Acknowledgments

First and foremost, I would like to thank my advisor, Dr. Seth Hubbard for allowing me the opportunities I have been afforded over the years and for agreeing to oversee the work toward this thesis. He has been paramount to my learning and understanding of the concepts discussed hereafter and has been a great mentor and advisor both through my undergraduate and graduate careers.

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Abstract

In this work, InAs quantum dots grown by organometallic vapor-phase epitaxy (OMVPE) are investigated for application in III – V material solar cells. The first focus is on the optimization of growth parameters to produce high densities of uniform defect-free quantum dots via growth on 2” vicinal GaAs substrates. Parameters studied are InAs coverage, V/III ratio and growth rate. QDs are grown by the Stranski-Krastanov (SK) growth mode on (100) GaAs substrates misoriented toward (110) or (111) planes with various degrees of misorientation from 0° to 6°. Atomic force microscopy results indicated that as misorientation angle increased toward (110), critical thickness for quantum dot formation increased with $\theta_c = 1.8 \text{ML}, 1.9 \text{ML}$ and $2.0 \text{ML}$ corresponding to 0°, 2° and 6°, respectively. Results for quantum dots grown on (111) misoriented substrates indicated, on average, that higher densities of quantum dots were achieved, compared with similar growths on substrates misoriented toward (110). Most notably, a stable average number density of $8 \times 10^{10} \text{cm}^{-2}$ was observed over a range of growth rates of $0.1 \text{ML/s} - 0.4 \text{ML/s}$ on (111) misoriented substrates compared with a decreasing number density as low as $2.85 \times 10^{10} \text{cm}^{-2}$ corresponding to a growth rate of $0.4 \text{ML/s}$ grown on (110) misoriented substrates. $p$-$i$-$n$ solar cell devices with a 10-layer quantum dot superlattice imbedded in the $i$-region were also grown on (100) GaAs substrates misoriented 0°, 2° and 6° toward (110) as well as a set of devices grown on substrates misoriented toward (111). Device results showed a $1.0 \text{mA/cm}^2$ enhancement to the short-circuit current for a
2° misoriented device with 2.2ML InAs coverage per quantum dot layer. Spectral response measurements were performed and integrated spectral response showed sub-GaAs bandgap short-circuit contribution which increased with increasing InAs coverage in the quantum dot layers from 0.04mA/cm²/ML, 0.28mA/cm²/ML and 0.19mA/cm²/ML corresponding to 0°, 2° and 6° misorientation, respectively.

The second focus of this study was on the OMVPE growth of InAs quantum dots in a large-area commercial reactor. Quantum dot growth parameters require careful balancing in the large-scale reactor due to different thermodynamic and flow profiles compared with smaller-area reactors. The goal of the work was to control the growth process in order to produce high densities of uniform quantum dots for inclusion in double and triple junction III – V material solar cells. Initial growth proved unsuccessful due to lack of familiarity with the process but through balancing of injector flows of alkyl gasses, coherent and optically active quantum dots were able to first be formed at low densities (0.5 – 0.7 × 10¹⁰cm⁻²). Further optimization included increased quantum dot growth times leading to number densities in the (2.1 – 2.7 × 10¹⁰cm⁻²) with improved optical performance as measured by photoluminescence (PL) spectroscopy. Finally, an investigation of GaAs spacer layer thickness for improved optical coupling was performed, indicating that a combined low temperature and high temperature GaAs thickness of 9.3nm led to strong PL intensity indicating good optical coupling of QD layers. Gel/(In)GaAs double junction solar cells were grown and fabricated with and without quantum dots in the (In)GaAs cell to investigate the effect of quantum dot inclusion on device performance. AM0 measurements showed an average increase of 1.0mA/cm² in short-circuit current for these devices. Integrated spectral response measurements revealed a contribution to
The short-circuit current of 0.02 mA/cm$^2/QDlayer$ which is consistent with reports seen in literature. The current improvement for the double junction solar cells motivated the investigation of quantum dot inclusion in the (In)GaAs junction of a Ge/(In)GaAs/InGaP triple junction solar cell. $AM0$ measurements on these cells did not reveal any increase in current for quantum dot enhanced devices over a baseline device. Integrated spectral response for each junction revealed an increase of 0.3 mA/cm$^2$ in current for the middle junction and the top junction, respectively, compared with baseline results for these junctions, but also that the InGaP top junction was current limiting. This potentially is due to poor material quality in the InGaP junction as a result of quantum dot inclusion in the junction beneath it or to strain effects resulting from quantum dot inclusion. This current limiting nature of the top junction may have led to a reduced efficiency for quantum dot devices compared with a baseline and further optimization is required in order increase the efficiency of the quantum dot device compared with a baseline device.
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Chapter 1

Introduction

1.1 SOLAR POWER: HUMBLE BEGINNINGS TO PRESENT DAY

Shortly after the demonstration of the photovoltaic effect in 1839 by Alexandre Edmund Becquerel, the first photovoltaic cell was built by coating selenium with a thin layer of gold [1]. However, this device performed with only about 1% power conversion efficiency. In the years to follow, different designs came about, owing their operational principles to the photoelectric effect, discovered by Heinrich Hertz in 1887 and later explained by Albert Einstein in 1905. The modern junction semiconductor solar cell was then patented in 1946 by Russell Ohl who discovered this structure while working on what would eventually lead to the transistor [2]. In 1954, at Bell Laboratories, the first diffused silicon $p$-$n$ junction solar cell was developed by scientists Daryl Chapin, Calvin Souther Fuller and Gerald Pearson [3]. Their device performed with a power conversion efficiency of 6%, which was significant as the cost to produce electricity was very high.

In 1958, a landmark satellite launch proved the value of photovoltaic cells when
Vanguard I launched on March 17. Vanguard I was the first satellite to include external solar cells, but was to be powered mainly by chemical cell batteries. The batteries failed shortly after launch, but the solar cells enabled the satellite to be powered for six years [4]. The huge success of the photovoltaic cells on this mission caused newer satellites designs to incorporate solar power as the primary power source.

Silicon photovoltaics are still the primary power source on the International Space Station due to the abundance of Si and ability for mass production. However, due to increased efficiency and mass specific power ($W/kg$) demands, research into $III – V$ materials for photovoltaic application began to gain popularity. As photovoltaic research effort increased and devices were able to be made more cheaply and more efficiently, the need arose for new materials useful in different applications. In the 1960s, the technique of organometallic vapor-phase epitaxy (OMVPE) was developed [5]. OMVPE enabled the mass production of high-quality, single-crystalline $III – V$ semiconductor materials. This was anticipated to produce high-efficiency photovoltaic devices and by the 1990s, large-scale production was underway [6].

1.2 ORGANOMETALLIC VAPOR-PHASE EPITAXY AND III-V COMPOUND MATERIALS

Organometallic vapor-phase epitaxy (OMVPE), also called metalorganic chemical vapor deposition (MOCVD), is a chemical vapor deposition process used for growing high quality crystalline semiconductor material. OMVPE has become a major process
in the growth and manufacturing of $III - V$, $II - VI$ and $IV - VI$ material opto-electronic devices [7]. Unlike molecular beam epitaxy (MBE), the OMVPE process takes place through chemical reactions of precursor materials as opposed to a physical deposition and occurs at much higher pressures ($70 - 760$ Torr, compared with $10^{-9} - 10^{-11}$ Torr). This is an advantage of OMVPE over MBE since the relative high pressures used during growth result in less down-time when pumping the chamber.

OMVPE has several other advantages over MBE (and other methods of epitaxy such as liquid phase epitaxy (LPE) and chemical beam epitaxy (CBE)) such as the capability for large-scale growth, extremely high purity and high growth rates of deposited materials as well as the selective growth of materials [8]. In fact, the early doubts of the purity of semiconductor materials produced by OMVPE were dismissed when reports of extremely high-purity gallium arsenide (GaAs) with low temperature mobilities greater than $100,000 cm^2/Vs$ were published by Seki et al. [9]. The development and demonstration of high-performance minority carrier devices in the 1970s and 1980s finally led to the rapid increase in research effort of OMVPE throughout the 1980s and 1990s [10]. Today, OMVPE has matured into the main epitaxy technique for the production of commercial devices.

OMVPE involves the flow of gaseous mixtures which contain the constituent molecules which are the precursors for epilayer growth. The standard precursors for OMVPE growth of $III - V$ materials like GaAs or InP are metalorganic sources containing group $III$ elements (i.e. alkyls). The group $V$ containing precursors are typically hydrides of arsenic or phosphorus. Purified hydrogen gas is used as a carrier gas.
Typical growth temperatures for this process are $550^\circ C - 700^\circ C$ due largely to the stable growth rates attained in this temperature regime. In this temperature range, the reaction rates of surface kinetics are sufficiently high that diffusion is the rate-limiting step for epitaxial growth. The growth rates can be controlled by adjusting the partial pressures of the gaseous precursors without change in temperature.

The CVD process involves four regions; they are the substrate, interface/growth, transport and carrier/source regions. The series of steps in the CVD process for epitaxial growth of GaAs is illustrated in figure 1.1. The gasses containing the required source elements flow into the chamber from the left, as seen in the figure.

![Figure 1.1: Schematic of OMVPE process.](image)

A concentration gradient of the TMGa and $\text{AsH}_3$ exists between the source and
interface regions, which causes diffusion of these molecules toward the substrate surface. The precursor molecules then undergo pyrolysis, whereby TMGa experiences homogeneous decomposition of methyl groups and AsH$_3$ experiences breaking of the hydrogen bonds. Ga and As then adsorb to the substrate where the individual species react kinetically to form the desired GaAs according to the chemical reaction given by

$$AsH_3 + (CH_3)_3Ga \rightarrow GaAs + 3CH_4$$

(1.1)

The precursor molecules are constantly supplied throughout the OMVPE process, however, at high growth temperatures, desorption occurs, as illustrated in figure 1.1. Because of this, the growth of compound semiconductor material by OMVPE requires an overpressure of the group $V$ material, like AsH$_3$, to prevent the decomposition of material at the substrate. The organic by-products such as $CH_4$ are transported from the interface region to the carrier gas and expelled from the reactor chamber as waste.

GaAs was one of the earliest materials to be developed by OMVPE and offers several advantages over silicon, which dominates the photovoltaic industry. GaAs, and many other $III - V$ materials, have a direct bandgap, compared with the indirect bandgap of silicon. This allows for the direct absorption of photons, leading to stronger absorption for GaAs over Si. Stronger absorption means that GaAs devices can be made thinner since most of the sunlight is absorbed within $\sim 2 - 3 \mu m$. This saves material cost and weight, which is an important factor for consideration when using PV devices in space. GaAs devices have also demonstrated improved radiation tolerance over Si devices [11–13], improving the device lifetime when subject to ionizing radiation.
experienced by satellites outside of shielding from the earth’s magnetic field.

The potential selection of materials for device application was greatly expanded with the advent of OMVPE technology. The material system was extended from single compound materials to a wide range of $III - V$ materials based on binary and tertiary compounds of Ga, In, Al, N, P, As and Sb, which could be grown epitaxially. Since OMVPE allows for abrupt layer growth, the precise deposition and alloy compositions of these $III - V$ compounds could be controlled, altering the bandgaps and thus, their electronic and photonic properties. Figure 1.2 is known as the crystal grower’s chart and displays a variety of $III - V$ compounds with their bandgaps and lattice constants [14].

![Figure 1.2: Bangap energy vs. lattice constant for common III-V semiconductors. [14]](image-url)
The plot gives some information on how alloying of different group III and V elements affects the bandgap of the compound as well as giving lattice constant information for different III – V binaries and terterials. Lattice constant is important when stacking epitaxial layers of different material since lattice mismatch can lead to strain-related defects. The figure outlines the lattice-matching condition for a state of the art triple junction solar cell with an (In)GaAs middle cell and InGaP top cell lattice-matched to the lattice constant of a Ge bottom cell, shown by the dashed box. This will be discussed in more detail in the next section, dealing with multijunction solar cell devices grown by OMVPE.

1.3 III-V PHOTOVOLTAICS: SINGLE AND MULTI-JUNCTION

1.3.1 Single-Junction GaAs Solar Cell Operation

The difference in energy between the CB and the VB is known as the bandgap ($E_g$) and in order to excite a charge carrier from the valence band to the conduction band for use in a circuit, energy at least equal to $E_g$ must be supplied. GaAs has a bandgap of 1.42eV which corresponds to a wavelength of $\sim 870\text{nm}$. This means that an incident photon of energy 1.42eV will successfully excite an electron to the CB for collection. The sun, however, outputs a broad spectrum of wavelengths which closely matches the spectral irradiance of a 6000K blackbody. A consequence of the single bandgap of GaAs (or any single bandgap solar cell) and the spectral range of the sun is shown in figure 1.3 as an energy band diagram with three different cases: $E_{\text{photon}} = E_g$, \[ E_{\text{photon}} = E_g, \]
$E_{\text{photon}} < E_g$ and $E_{\text{photon}} > E_g$. Illustrated in the figure are two intrinsic loss mechanisms for a solar cell. When $E_{\text{photon}} < E_g$ (red), the incident photon does not possess sufficient energy to excite an electron across the bandgap. As a result, the device is transparent to the photon and it passes through the cell. This is called transmission.

![Figure 1.3: Energy band diagram of a p-n junction solar cell showing absorption (green), transmission (red) and thermalization (blue).](image)

The second intrinsic loss depicted in figure 1.3 is the case where $E_{\text{photon}} > E_g$ (blue). For these high-energy photons, excitation to the CB occurs, but the electron is in a higher CB energy state initially and must relax to the band edge in order to minimize its energy. This causes the excess energy to be given off as heat through lattice vibration or phonons and is called thermalization. Altogether, about 55% of incident solar power is not usable by a PV device due to thermalization and transmission [15].

Due to the intrinsic nature of the two loss mechanisms outlined, along with other
intrinsic loss such as Boltzmann loss [16], a landmark paper published in 1961 by William Shockley and Hans Queisser reported the maximum theoretical efficiency for a single bandgap solar cell device based on a detailed balance calculation [17]. Detailed balance is a principle which states that any body which absorbs energy (light) must also emit energy. Since a photovoltaic device emits more light when optically excited due to radiative recombination, the power conversion efficiency of the cell is limited [18]. Shockley and Queisser found that, under thermodynamic balance, the maximum attainable efficiency under one-sun illumination was 33.1% and corresponded to a bandgap of $\sim 1.1eV$, the bandgap of silicon. This limit became fundamental in solar cell production and is known as the Shockley-Queisser limit. Despite the maximum efficiency of 33.1% for a silicon cell, modern state-of-the-art single crystal silicon devices perform at around 24% under one-sun illumination [19,20]. Due to the direct bandgap of GaAs and its strong photon absorption along with various PV advances such as photon recycling, world record single junction devices have been reported, performing at 28.8% efficiency [21], coming close to the theoretical maximum.

1.3.2 Multi-junction Solar Cells

Single bandgap photovoltaic devices are limited in their ability to effectively convert a wide range of the solar spectrum into usable energy due largely to loss by transmission and thermalization. There have been several attempts to increase power conversion in PV devices in recent years, one of which is the multi-junction solar cell [22]. The structure of a multi-junction solar cell requires the epitaxial growth of two or more $III - V$
materials of different bandgap, each electrically connected by tunnel junctions. The wider bandgap materials at the top of the stack serve to filter the shorter wavelength light by absorption while less energetic photons pass through to the lower junctions whose bandgaps are more sensitive to those wavelengths. With appropriate selection of materials, this structure reduces the loss due to thermalization as well as transmission, leading to higher power conversion efficiencies. The current state-of-the-art triple junction solar cell (TJSC) design is shown in cross section in figure 1.4. This type of device consists of a Ge bottom cell \( (E_g = 0.70\text{eV}) \), an (In)GaAs middle cell \( (E_g = 1.4\text{eV}) \) and an InGaP top cell \( (E_g = 1.8\text{eV}) \) connected by tunnel junctions as shown to the right of the figure.

![Figure 1.4: Left: Absorption of each layer in the TJSC compared with the AM0 solar spectrum. Right: Cross section of a state-of-the-art triple junction solar cell.](image)

To the left of figure 1.4, a plot of the \textit{AM0} solar spectrum is shown, overlaid with the power conversions of each junction in the TJSC device, calculated by detailed balance. Thermalization still occurs, represented by the white area between the \textit{AM0} spectrum...
and the spectral irradiances of the junctions, but compared with a single-junction GaAs device (here, the middle junction), its effect is reduced. Also, the absorption of the TJSC has been extended to $\sim 1.7\mu m$ by the inclusion of the Ge junction, compared with the absorption cutoff of $0.87\mu m$ for the single junction GaAs device. Thus, loss due to transmission is reduced by the use of multiple junctions. Modern TJSC devices have been reported performing at around 33% efficiency under one-sun illumination [23].

The selection of materials with appropriate bandgap is important when designing a multi-junction solar cell device, however, a major constraint when selecting the material system is the lattice-matching condition. Growth of material by epitaxy can be either strained, by lattice-mismatching the epilayer and the substrate or not strained, by lattice-matching the epilayer to the substrate. Lattice-mismatching, or growth of material with a different lattice constant than the substrate leads to strain-related defects, such as misfit dislocations, which degrade the performance of the device. Thus, the material system for the multi-junction solar cell shown in figure 1.4 is limited by the single lattice constant of the Ge substrate, which was illustrated in figure 1.2.

A second constraint which limits the performance of a TJSC is the current-matching condition. Since the three sub-cells are connected in series, the current through each cell must be constant. For this to be true, the entire device must output current equal to the smallest sub-cell current. Integration of the sub-cell responses in figure 1.4 indicates that the GaAs junction is the current-limiting junction in the TJSC shown. Since output power is the product of current and voltage, in order to produce more power, a higher current should be output. Higher voltage should also be produced,
but the change in voltage of the device is less dramatic, since in a series circuit, the
voltage across each resistive load adds. Unfortunately, the lattice-matching condition
makes the selection of different materials difficult without introducing unwanted strain
in the device.

There have been several proposed methods to improve device efficiencies beyond
33%. Some of these include growth of four and five junctions [24, 25] which further
increase absorption and reduce intrinsic loss in the device. The challenge which
exists for inclusion of more junctions is the lattice-matching constraint which makes
the growth of material with both an appropriate bandgap and lattice constant difficult.
However, Y. Masafumi et al. and others have reported theoretical device efficiencies
for four-junction devices of over 40% under one-sun illuminations [24]. Another method
is the inverted metamorphic (IMM) solar cell design which allows the growth of lattice-
mismatched materials whose bandgaps are closer to the ideal bandgap for a multi-
junction device with bottom-cell $E_g = 1.0eV$ [26]. Such devices have been reported to
perform with 40.7% efficiency under a concentrated terrestrial spectrum [27].

Another method for improving device efficiency, which is the focus of this work,
is known as bandgap engineering. Bandgap engineering is a method by which the
effective bandgap of a sub-cell in the TJSC stack is altered through the inclusion of
nanostructures such as quantum wells (QWs) or quantum dots (QDs), without affect-
ing the lattice-constant, thereby increasing the sub-cell current, and thus the overall
device performance. Essentially, by lowering the bandgap of the subcell, its absorption
can be extended to longer wavelengths, thus "stealing" photons from the current-rich
bottom cell. This would result in a higher matched current through each subcell and thus a higher output power from the device. Quantum dot bandgap engineering has been extensively investigated at RIT in recent years [28]. Figure 1.5 shows the result of a detailed balance calculation as a contour plot indicating the efficiency for a TJSC with a Ge bottom cell and varied top and middle cell bandgaps. The x-axis represents the varied bandgap for the middle cell and the y-axis represents the varied bandgap for the top cell. The contour lines are those of constant efficiency.

![Contour plot of efficiency versus top cell and middle cell bandgap for a TJSC structure with fixed Ge bottom cell indicating benefit of bandgap engineering.](image)

The figure indicates the power conversion efficiency of 33% for the TJSC structure shown in figure 1.4 corresponding to a middle cell bandgap of 1.42\(\text{eV}\) and a top cell bandgap of 1.85\(\text{eV}\). The plot shows, however, that a lower middle cell bandgap can result in a power conversion efficiency of over 47% at one-sun illumination. A more
detailed discussion of nanostructures is made in the next section as well as in the next chapter on quantum dots.

1.3.3 Nanostructured Photovoltaics & Intermediate Band Solar Cells

As discussed in the last section, the lattice-matched TJSC design is limited in its efficiency by the GaAs current-limiting junction, but through bandgap engineering, current through this junction and thus the overall power output by the device can be increased. Bulk materials are only effective absorbers of light up to the band edge, whereafter, a sharp cutoff in absorption exists and the device becomes transparent to less energetic photons. The inclusion of a narrow bandgap material in the bulk material can extend its absorption to longer wavelengths to convert more of the solar spectrum into usable energy.

In 1972, while working at Bell Labs, Charles H. Henry proposed that the inclusion of very thin heterostructures (quantum wells) could lead to quantum confinement of electrons and thus, states within the bandgap of the host material. In 1973, Henry’s design for a double heterostructure was demonstrated by showing sub-bandgap ($E_{\text{photon}} < E_g$) absorption peaks and subsequently the investigation into nanostructured optoelectronic devices began [29]. The first quantum confining structures were used in the investigation of quantum well lasers, but in recent time, quantum well and quantum dot inclusion in solar cell devices has gained popularity as a method for increasing current output for multi-junction solar cells as well as the realization of the intermediate band solar cell (IBSC), proposed by Luque and Marti [30]. The IBSC structure relies on
strong coupling of quantum dot states leading to the strong spatial overlap of electron wave function for the formation on an intermediate energy band within the bandgap of the host material. A simplified energy band diagram for an IBSC is presented in figure 1.6. The figure shows the valence and conduction bands along with an intermediate energy band within the bandgap of the host material. The figure indicates valence band to intermediate band transitions ($E_{IV}$), intermediate band to conduction band transitions ($E_{CI}$) and valence band to conduction band transitions ($E_{CV}$) as well as the chemical potentials for quasi fermi levels $\mu_V$, $\mu_I$ and $\mu_C$.

![Energy band diagram](image)

Figure 1.6: Energy band diagram for an intermediate band solar cell indicating valence band to intermediate band transitions ($E_{IV}$), intermediate band to conduction band transitions ($E_{CI}$) and valence band to conduction band transitions ($E_{CV}$).

The IBSC device design has been proposed to far exceed the performance of even multijunction devices [31–33]. Figure 1.7 shows the result of a detailed balance calculation for an IBSC under concentration as a contour plot of efficiency. The x-axis
represents varying the intermediate band to conduction band energy \( (E_{CI}) \) and the y-axis represents varying the intermediate band to valence band energy \( (E_{IV}) \). The plot indicates that under a concentrated terrestrial spectrum, an IBSC exhibits a maximum theoretical efficiency of over 60% compared with 33% predicted by Shockley and Queisser.

![Figure 1.7: Detailed balance efficiency plot for an IBSC under 1000 sun concentration.](image)

The focus of the work in this thesis is largely the control of QD properties such as size, shape and ordering through careful control of growth parameters in the OMVPE reactor for the eventual realization of an IBSC device. Additional motivation for this work is the theoretical benefit of bandgap engineering, shown in figure 1.5. Presented in this thesis is an investigation of the benefit of quantum dot inclusion in GaAs solar cells for current enhancement as well as their inclusion in the GaAs junction of a state-of-the-art TJSC device for improved power conversion efficiency. A more detailed discussion of quantum dots and other nanostructures is made in chapter 3.
1.4 ORGANIZATION OF WORK

The following chapters of this thesis focus on the growth and characterization of InAs quantum dots by OMVPE as well as the characterization of quantum dot enhanced single and multijunction $III - V$ solar cells. Chapter 2 is an experimental procedures chapter, focusing on the underlying and operational principles of the characterization techniques used throughout this thesis. It should serve as a technical report and does not present any material or device results. Chapter 3 focuses on the characterization of OMVPE grown InAs quantum dots in a small-area Veeco P125LDM reactor at the NASA Glenn Research Center for the realization of an IBSC. A discussion of the motivation and theory of nanostructure physics is presented in chapter 3 along with morphological and optical results for quantum dots grown with different growth parameters and device results for quantum dot enhanced single junction GaAs solar cells. Chapter 4 focuses on the optimization of InAs quantum dot growth in a large-area OMVPE reactor as well as the characterization of quantum dot enhanced double and triple junction solar cells. Chapter 5 presents conclusions for both small and large-area reactor quantum dot growth, solar cell performance as well as a discussion on related future work.
Chapter 2

Experimental Procedures

The characterization of samples investigated in this study is separated into two categories. They are a) characterization of InAs QD test structures grown on GaAs substrates to determine the effect of varying OMVPE growth parameters and b) characterization of QD enhanced single and triple junction solar cells with similarly grown QDs to quantify their effect on solar cell performance. Thus, the testing apparatuses and methodologies used herein satisfy two purposes: materials characterization for InAs QD test structures to quantify QD statistical, optical, morphological and bulk properties, and solar cell device testing to extract performance parameters. This chapter will serve as the generic basis for all of the testing methodologies used as well as to provide a technical description of the operating principles behind the measurement techniques performed.
2.1 MATERIALS CHARACTERIZATION METHODS

2.1.1 Atomic Force Microscopy

The main method for quantifying changes due to growth processes is to directly observe and measure the features grown. While it is possible to get *in-situ* measurements of the surface during MBE growth using techniques like reflection high-energy electron spectroscopy (RHEED) [34,35], obtaining similar measurements during MOCVD growth is slightly more difficult, and so a post-growth method is typically used in order to make direct measurement. Directly accessing structural information of features is essential to the understanding of the growth process and microscopy is typically used to observe morphological properties. However, when the size of the features is extremely small, optical microscopy becomes quickly insufficient for their direct observation. This is the case for quantum dots, whose size is on the nanometer scale.

In 1986 at IBM, Binnig, Gerber and Quate invented the atomic force microscope (AFM) which was based on the technology previously used in the scanning tunneling microscope (STM) [36]. A benefit of the AFM over STM is that the sample surface does not need to be conducting, and thus AFM has a different range of applications. AFM is a scanning probe microscopy (SPM) technique, the basic operating principle of which relies on Van der Waals and atomic forces between an atomically fine probe tip, usually with tip radius of a few nanometers, and the sample surface.

There are two primary modes of operation for an AFM, contact mode and tapping mode. In contact mode, AFM tip is dragged across the surface of a sample and
its vertical deflection is measured, tracking the contours of the surface. Near the surface, the short-range attractive forces are very strong, and thus the contact mode is preferred to a non-contact mode where strong attractive forces cause the cantilever to snap-in to the surface. In contact mode AFM, the force between the probe tip and the surface is kept constant by maintaining a constant cantilever deflection, controlled externally by an electronic feedback loop. From the movement of the cantilever, a topographical map of the surface is generated which is a digital image of the sample surface.

The second operational mode, which is the method used in this work, is known as the tapping mode. This technique is quite similar to operation in the contact mode with the difference being that the cantilever oscillates very close to its resonant frequency, typically in the tens to hundreds of KHz range, above the sample surface. This oscillation produces a laser strip which is reflected by a mirror onto a double-photodetector array. A schematic of an AFM operating in the tapping mode is shown in figure 2.1.

The array is calibrated so that $V_A - V_B = 0$. When a feature on the sample surface is encountered by the tip, the oscillations are dampened due to Van der Waals forces or other close-range forces, or enhanced in the presence of a valley, changing the detector reading. This change in voltage is fed into the feedback loop as shown in figure 2.1, which signals the precise elongation or contraction of a piezoelectric device underneath the sample surface. Based on the contraction or elongation, a topographical image of the sample surface is again generated. A representative atomic force micrograph of a QD sample used in this study is given in figure 2.2, with the
Figure 2.1: Schematic of the operation of an atomic force microscope in the tapping mode.

Yellow features distributed throughout being the quantum dots. Evident by the scale bar inserted in the image, the feature size is typically less than 20 nm.

Tapping mode AFM is preferred over non-contact AFM since, under normal ambient conditions, moisture tends to form in a very thin layer on the sample surface which makes it difficult to bring the probe tip close enough for short-range forces to be detectable while preventing the tip from sticking. It is preferred over contact mode because less damage is sustained by the sample surface and the tip due to the gentleness of operation in the tapping comparatively. Thus, tapping mode AFM can be used to image very soft materials and results can remain constant over a much longer time range than is possible in contact mode [37].

For samples in this study, a Veeco D3100 multimode atomic force microscope was used in the tapping mode. Nanoscope III software was used to control the tool and
select scan parameters. For scans presented, the tip used was a Veeco OTESPA tip was used which provided high lateral resolution. The tip diameter at its finest point was nominally $10\,\text{nm}$ which was sufficient for imaging nanostructures with lateral dimension on the order of $20 – 30\,\text{nm}$ like those investigated in this work. From the data collected by AFM measurement, statistical properties such as nanostructure height, diameter, number density and volume can be extracted using metrology software. For the work performed for this thesis, Scanning Probe Image Processor (SPIP) software from Image Metrology was used. SPIP Data from successive experiments is given in the following chapters where analysis of results is made.

2.1.2 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a nondestructive, non-contact method used to probe the electronic structure of materials. The intensity and wavelength of emitted
photoluminescence provide direct insight into material properties such as the determination of bandgap, impurity levels and defect detection, and recombination mechanisms. The bandgaps present in a material can be directly measured by PL according to the wavelengths of photons emitted through radiative recombination of charge carriers. A photon’s energy is related to its wavelength according to $E_{\text{photon}} = \frac{hc}{\lambda}$.

A schematic of the radiative and non-radiative processes associated with PL is presented in figure 2.3. The figure illustrates three processes which make up photoluminescence spectroscopy. They are a) photoexcitation of electrons to the CB by photons of energy greater than $E_g$, b) non-radiative relaxation to conduction band edge through repeated lattice vibrations and c) spontaneous radiative recombination of charge carriers. Process (b), illustrated in the figure, occurs quickly, on the order of picoseconds ($10^{-12}$ s). Process (c) takes place a bit more slowly, in the nanosecond to microsecond range ($10^{-9}$ – $10^{-6}$ s).

Figure 2.3: Energy band diagram for photoluminescence spectroscopy showing radiative recombination.
In addition to bandgap determination of bandgaps by PL, low temperature measurements can reveal spectral peaks which are associated with impurities contained within the host material. Additionally, the intensity of emitted PL is directly related to the relative amount of radiative and non-radiative events. Since non-radiative processes are associated with defects and impurities, PL can be used to qualitatively monitor changes in material quality as a function of growth and device processing conditions.

A block diagram of the test setup used in this work is shown in figure 2.4. A 300W/cm² Ar⁺ ion 514nm laser was used for photoexcitation of the sample at room temperature. A 0.5m HoribaJY iHR320 monochromator with a cooled InGaAs detector was used to measure signal. In order to ensure accurate PL measurements, the laser signal was chopped at a rate of 167Hz and the monochromator was coupled to a lock-in amplifier to remove lower-frequency noise. Horiba SynerJY software was used to record the signal and display PL spectra.

2.2 SOLAR CELL OPERATION & TESTING METHODS

2.2.1 Solar Cell Fundamentals

Fundamentally, a solar cell is p-n junction diode, similar to an LED or transistor. When the solar cell is illuminated with light of photon energies greater than or equal to $E_g$, an electron-hole pair (EHP) is generated. After diffusion to the junction, charge separation occurs due to the built-in electric field. The current injected by the incident light can be represented by $I_L$. When connected to an external load, a solar cell develops a
potential difference between terminals. The potential difference generates a current which acts in the opposite direction to the induced photocurrent. This reverse current is called the dark current and behaves similar to the current characteristic of a diode with an applied bias. For an ideal diode under forward voltage bias with no illumination the dark current, $I_{dark}$, varies according to the ideal Shockley diode equation as

$$I_{dark}(V) = I_0 \left( e^{\frac{qV_{app}}{k_BT}} - 1 \right)$$

(2.1)

where $I_0$ is the reverse saturation current, $q$ is the electronic charge, $V_{app}$ is the applied voltage bias, $k_B$ is Boltzmann’s constant and $T$ is the absolute temperature in kelvin. Conventionally, photocurrent is taken to be positive, so the net current through the cell is the difference between the light-injected photocurrent, $I_L$, and the dark current, $I_{dark}$. The total current through a solar cell under illumination is thus
\[ I_{\text{cell}}(V) = I_L - I_D \left( e^{\frac{qV_{\text{app}}}{kT}} - 1 \right) \] (2.2)

The point at which no voltage is applied is called the short-circuit condition, similar to that of an electrical circuit. At short-circuit conditions, the second term in equation 2.3 vanishes and the total current through the solar cell is simply the short-circuit current, \( I_{\text{sc}} \). Thus \( I_L = I_{\text{sc}} \) at short-circuit. Figure 2.5 (left) shows the current-voltage \( I-V \) characteristic for a solar cell under forward bias both in the dark and illuminated.

The effect of the induced photocurrent at the short-circuit condition is that the \( I-V \) curve is shifted into the fourth quadrant by an amount equal to \( I_{\text{sc}} \) as shown in the figure. This is known as the power quadrant because it is the operating region where power is generated. As previously stated, the usual sign convention is that photocurrent is taken to be positive, so the illuminated diode \( I-V \) characteristic is flipped into the first quadrant to demonstrate that the solar cell is generating power. This is shown in figure 2.5 (right).

As bias is increased, the diode forward operation current (\( I_{\text{dark}}(V) \)) begins to balance out the photocurrent. At a certain applied forward bias, \( I_L - I_{\text{dark}}(V_{\text{app}}) = 0 \). This voltage bias point is called the open-circuit voltage (\( V_{\text{oc}} \)), similar to that for an electrical circuit. \( V_{\text{oc}} \) is indicated on the righthand plot in figure 2.5 as the intercept to the voltage axis. The power out of the solar cell can be calculated for any coordinate pair of voltage and current in the plot shown in figure 2.5 by taking the product of the two. In other words \( P = IV \). Total power is plotted on the same set of axes in the righthand plot in the figure, represented by the blue curve. The point at which the maximum
power is generated is called $P_{\text{max}}$ and is given by the product of some current ($I_{\text{max}}$) and voltage ($V_{\text{max}}$) which maximizes this quantity. This is the operating point for a solar cell and is indicated at the knee of the power curve in figure 2.5. Fill factor which is roughly a measure of the squareness of the $I-V$ curve is calculated from $P_{\text{max}}$ as the ratio

$$FF = \frac{P_{\text{max}}}{I_{\text{sc}} \cdot V_{\text{oc}}} = \frac{I_{\text{max}} \cdot V_{\text{max}}}{I_{\text{sc}} \cdot V_{\text{oc}}}$$ \hspace{1cm} (2.3)$$
or the ratio of areas of the grey square to the green square illustrated in figure 2.5.

The most important solar cell parameter is the power conversion efficiency. Efficiency is a measure of the ratio of the work or power output by the device to the amount of work or power put in by an outside source. Solar cell efficiency, $\eta$, can be calculated using the expression
\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{I_{\text{sc}} \cdot V_{\text{oc}} \cdot FF}{P_{\text{in}}} \]  

(2.4)

where \( P_{\text{in}} \) for a solar cell is \( P_{\text{sun}} \) and the normalized irradiance changes depending on the spectrum to which the cell is exposed. Solar spectra are discussed in the next section.

2.2.2 Solar Cell Testing Methods

Testing of photovoltaics is done under a well defined standard spectrum, which can be different depending on the conditions under which the device is to be used. The sun’s spectrum closely matches the spectral irradiance of a 6000K blackbody and is often modeled as such. The solar spectrum changes as the angle of the sun changes with respect to earth’s zenith. The optical path length that the sun’s light must pass through is known as the air mass and depending on where and when a solar cell is tested under an incident solar spectrum, a different air mass value must be used. Figure 2.6 shows the standard AM0, AM1.5G and AM1.5D solar spectra, with a 6000K blackbody spectrum as a reference. AM0 represents the solar spectrum incident at the edge of the Earth’s atmosphere, or under zero air-mass. AM1.5 represents the spectrum with the sun making an angle of 48.2° with respect to the Earth’s zenith, or under 1.5 air-mass. AM0 is the standard spectrum for testing photovoltaic devices under space conditions and AM1.5 is the standard spectrum for testing devices for terrestrial application. The dips in the AM1.5 spectra shown in figure 2.6 arise due to absorption in the atmosphere. Since AM0 is a measure of the irradiance at the edge
of the Earth’s atmosphere, these absorption and scattering effects are not observed.

Figure 2.6: AM0 and AM1.5 solar spectra compared with a 6000K blackbody spectrum.

In order that solar cell testing results be consistent between different labs and manufacturers, a set of standards has been measured by the National Renewable Energy Lab (NREL) [38] so that solar simulators can be calibrated to whichever spectrum is necessary for a particular test. Samples tested in this work were done using a TS Space Systems (TSS) dual-source solar simulator calibrated to closely match the ASTM standard for both AM0 and AM1.5 spectra. A schematic of the solar simulator setup is given in figure 2.7. The setup consisted of a 6kW hydrargyrum medium-arc
iodide (HMI) lamp which provided the visible and ultraviolet part of the spectrum, and a 12kW quartz-tungsten halogen (QTH) bulb which provided the near infrared (NIR) and infrared (IR) part of the spectrum. Also shown in the figure are several shaping filters as well as a dichroic mirror to shape and combine the spectra of the two lamps. A plane full spectrum folding mirror was used to direct the combined spectrum toward the sample stage for illumination of the device under test.

Figure 2.7: Block diagram of TS Space Systems solar simulator at RIT.

The two lamps were calibrated under AM0 conditions using an InGaP₂ and a GaAs reference cell provided by NASA Glenn Research Center. The InGaP₂ reference cell was used for calibration of the HMI lamp since the cut-on wavelength of the QTH lamp is past the band edge of InGaP. The GaAs reference cell was then used to
calibrate the QTH lamp due to its strong response in the NIR region of the spectrum. A calibrated TSS AM0 spectrum is shown in figure 2.8 overlaid with the ASTM standard AM0 spectrum. The spikes in the TSS spectrum, shown in the figure, can be further smoothed by the inclusion of additional filters in the system, but it is clear that the two spectra are a close spectral match.

![Figure 2.8: TSS simulated AM0 compared with the ASTM standard AM0 spectrum.](image)

### 2.2.3 Spectral Responsivity and Quantum Efficiency

An key parameter when characterizing a solar cell’s performance under different test conditions is the cell’s quantum efficiency \( Q(E) \). \( Q(E) \) is a measure of the probability that an incident photon of energy \( E \) will deliver one electron to the external circuit. A
strength of QE as a metric for solar cell device and material characterization is that it does not depend on the incident spectrum. Instead, it depends the absorption coefficient of the solar cell material, the efficiency of charge separation and the efficiency of charge collection in the device [18]. Thus, $QE$ is directly related to the solar cell material quality and device design.

Detailed balance calculations predict device performance for a given set of test conditions, but make several assumptions to simplify the model, for example, that every incident photon creates a charge carrier for use in the circuit. In an actual device, not every incident photon results in a collected charge carrier, so the $QE$ is rarely equal to unity at any specific wavelength. $QE$ can be either directly measured or modeled in terms of the solar cell device’s spectral responsivity ($SR$), which is a measure of the amount of current ($A$) per unit power ($W$) illuminating the device at a given wavelength, $\lambda$. A model developed by H. Hovel and J. Woodall [39] based on a series of carrier transport equations which can be used, along with absorption data for a material to model current collection in a device. External quantum efficiency ($EQE$), which is the ratio of collected charge carriers to the number of incident photons of a given energy can calculated from measured $SR$ as

$$EQE(\%) = SR \times \frac{hc}{q\lambda} \quad (2.5)$$

where $SR$ is the cell’s spectral responsivity at a particular wavelength, $h$ is planck’s constant, $c$ is the speed of light in a vacuum, $q$ is the electronic charge and $\lambda$ is the wavelength.
Figure 2.9 shows, as an example, the spectral responsivity, reported as external quantum efficiency for a bulk GaAs \textit{p-i-n} solar cell. The dotted line in the figure represents the band edge of GaAs at $870\text{nm}$. As discussed in chapter 1, bulk materials are only effective absorbers of light up to the band edge, whereafter a sharp cutoff in absorption exists. This is illustrated in figure 2.9 with a sharp decrease in spectral responsivity for GaAs. At wavelengths beyond $870\text{nm}$, very little to no incident light causes any current out of the device. The GaAs device is transparent to photons of longer wavelength than $\lambda_{g,GaAs}$.

![Figure 2.9: External quantum efficiency for a GaAs \textit{p-i-n} solar cell device.](image)

$SR$ can also be used to calculate a solar cell’s short circuit current under any incident spectrum. To measure $I_{sc}$ directly for a given spectrum, a solar simulator is
required and in order that the data be reliable, the simulator must have a low degree of spectral mismatch from the lamps and filters used to create the spectrum. However, solar spectrum data is available for a wide range of different conditions. Using this available data, and the measured $SR$ of the solar cell, $I_{sc}$ can be calculated by integrating the $SR$ convolved with whichever spectrum is appropriate for the test conditions. Integrated $I_{sc}$ is calculated as

$$I_{sc} = \int_{\lambda_1}^{\lambda_2} SR(\lambda) \ast \phi_{\text{spectrum}}(\lambda) d\lambda$$  \hspace{1cm} (2.6)

where $SR(\lambda)$ is the measured spectral response and $\phi_{\text{spectrum}}(\lambda)$ is the desired solar spectrum.

Figure 2.10 gives a block diagram of the test setup used for SR measurements in this thesis. SR is measured using an Optronics Laboratories (OL) 750 monochromator, an optical chopper, a lock-in amplifier and source meter as shown in the figure. A tungsten bulb provides the required spectral bandwidth and diffraction grating is used to step through wavelengths for solar cell illumination at desired increments. Due to low signal intensities, an optical chopper coupled to a lock-in amplifier is used in order to provide noise-free amplification of the output signal. The solar cell is held at short-circuit current conditions and illuminated in order to measure the response for a given wavelength. Results are then normalized to a calibration run in order to accurately measure SR.
Figure 2.10: Block diagram of a Spectral Responsivity setup.
Chapter 3

Quantum Dot Growth on 2” Gallium Arsenide Substrates

3.1 NANOSTRUCTURES IN PHOTOVOLTAICS

3.1.1 Theory

Nanostructures, such as quantum wells (QW), quantum wires (QWR) and quantum dots (QD) are structures with at least one dimension on the nanometer ($10^{-9}m$) scale. Their size in this dimension is on the order of the de Broglie wavelength of an electron in that material (40nm for bulk InAs [40]), resulting in quantum confinement in that dimension. Quantum confinement of electrons (and holes) leads to a change in the density of available states in the material which has a pronounced effect on the electronic properties of the structure. Figure 3.1 shows the density of states versus energy for a bulk material and then the varying degrees of quantum confinement for each type of nanostructure with electron movement confined to two dimensions for a QW, one dimension for a QWR and zero dimensions for a QD. As shown in the figure,
the density of states function shifts from a parabolic shape in the bulk material to a more discrete or atom-like set of states for the QD.

Figure 3.1: Density of states for bulk material as well as for nanostructured materials.

QWs, QWRs and QDs are used in lasers, photodetectors and solar cells due to their tunability of optical and electronic properties [41]. A benefit of the inclusion of indium arsenide (InAs) QDs in the host material of a solar cell, such as GaAs is that their narrower bandgap (0.35eV for bulk InAs compared with 1.42eV for GaAs) allows lower energy photons which could not previously be absorbed, to now be absorbed by the QD layer and a secondary photon can excite the electron into the conduction band for current collection. Furthermore, carriers can escape the QD potential by tunneling or by thermal escape which was not possible for a device without QDs. These escape mechanisms for charge carriers can result in higher short-circuit current
for PV devices [42, 43].

The typical design for a QD enhanced solar cell is to include the QDs in the intrinsic or undoped region of a $p-i-n$ structure device. The band structure of such a device is shown in figure 3.2, illustrating the secondary escape mechanisms for a carrier in a QD state. Recall that previously (figure 1.3), the low energy (red) photon was transmitted through the solar cell and current was lost as a result. Thus, the inclusion of InAs QDs can extend the absorption of a GaAs $p-i-n$ solar cell.

Figure 3.2: Energy band diagram of a GaAs $p-i-n$ structure with InAs QDs imbedded in the intrinsic region.
3.1.2 Quantum Dot Self-Assembly

In this study, InAs quantum dots were grown by OMVPE at the NASA Glenn Research Center (GRC). InAs growth is similar to the growth of GaAs, given by equation Equation 1.1, with trimethylindium (TMIn) as the group III precursor, as opposed to TMGa. InAs QD growth occurs at lower temperature than GaAs growth (470°C compared with 600°C) due to the high mobility of the indium species. Growth temperatures too high in excess of 500°C can result in the desorption and dissolution of InAs from the substrate surface [44]

There are several types of heteroepitaxial growth modes, each resulting from different interfacial energies and substrate mismatches. Some of these are Frank-Van der Merwe (FW), or layer-by-layer growth, Volmer-Weber (VW), or 3D island formation, and Stranski-Krastanov (SK), or wetting layer to 3D island growth [45]. Equation 3.1 gives the condition for layer-by-layer growth to occur as

\[ \Delta \gamma = \gamma_A + \gamma_i - \gamma_B \leq 0 \]  

(3.1)

where \( \gamma_A \) and \( \gamma_B \) are the surface free energies of species A and B respectively, and \( \gamma_i \) is the interfacial free energy.

FW growth (2D) occurs in systems where the energies of the epilayer and interface sum to a lower energy than the substrate, in other words, the deposited material and substrate material are lattice-matched and equation 3.1 is satisfied [46]. In such systems atoms wet the surface and form smooth fully formed layers. VW growth
(3D) occurs in systems whose epilayer and interface energies sum to a greater energy than the substrate. In other words the deposited material and the substrate are lattice-mismatched. VW growth occurs in systems which the lattice constant, $a$, of the epilayer and the substrate are highly lattice-mismatched ($\frac{a_{\text{epi}}}{a_{\text{sub}}} > 10\%$) resulting in strain-induced 3D island formation as well as plastic deformation of the crystal, resulting in a high density of interfacial misfit dislocations [47]. The SK growth mode is an intermediary type of growth, characterized as a 2D to 3D type of growth [48] and is the growth method of QDs in this study.

SK growth occurs when the substrate and deposited material are slightly (<10%) lattice-mismatched. For an InAs/GaAs material system, a 7.2% mismatch exists. In these systems, monolayers (half of the lattice constant, $\sim 3\text{Å}$ for InAs) of InAs are grown directly on the substrate where the larger-lattice-constant InAs molecules compress so that their lattice constant matches that of the GaAs substrate below, thus compressively straining the epi-layer. This, however can only occur for very thin layers of InAs as strain continues to increase throughout the deposition. At a certain InAs layer thickness, $\theta_c$, called the critical thickness, deposition of more InAs results in a change from adhesion of material to the substrate to cohesion of adsorbed molecules. Through this process, the InAs molecules volumetrically relax to their natural lattice constant and newly deposited InAs bonds preferentially to the newly formed clusters as it is more energetically stable. The end result is the formation of coherently strained 3-D islands which are called quantum dots. The SK growth process is shown schematically in figure 3.3.
The process outlined in figure 3.3, however, doesn’t truly represent the structure depicted in figure 3.2 which shows multiple potential wells, or quantum dots in the $i$ region of a $p-i-n$ device. Figure 3.3 can be thought of as the process for growing each layer individual layer of QDs, but typical optoelectronic application usually requires the growth of a stack of QD layers for electronic coupling and signal amplification [49]. The growth of a stack requires careful considerations in the growth process, outlined in the next section.
3.1.3 Stacked QD Layers & GaP Strain Compensation

The growth of multiple layers of InAs QDs in a GaAs host requires the growth of GaAs spacer layers between InAs layers. The thickness of the spacer is typically only a few nanometers and is split into low temperature (LT) GaAs and high temperature (HT) GaAs layers. LT GaAs is grown at the same temperature as the QD layer and serves to cap the QDs, preventing dissolution of InAs as temperature is later increased. GaAs grown at this low temperature tends to be lower crystal quality material. The HT layer is then grown and acts as the GaAs surface on which the next layer of QDs is grown. This layer is grown at high temperature to maintain good crystal quality in that layer. InAs growth on GaAs, however, leads to compressive strain in the InAs layer and growing multiple layers in the InAs/GaAs system leads to the buildup of strain through the structure and eventually results in the formation of dislocations.

A method proposed by Hubbard et al. [50] to mitigate the build-up of compressive strain in order to grow multiple layers of defect-free InAs QDs on GaAs is to grow a thin layer of GaP between spacer layers. The lattice constant of GaP is a 3.6% tensile mismatch to that of GaAs (compared with the 7.2% compressive mismatch for InAs/GaAs). The thickness of the GaP layer must be carefully controlled in order that tensile strain effectively compensates the compressive QD strain. A modified continuum elastic theory (CET) model was developed by Bailey et al. to determine the thickness of the GaP layer for a given density and size of quantum dots, that results in the minimum overall superlattice stress [51]. This led to an optimum GaP thickness for a given set of growth parameters. GaP strain compensation was shown to improve
quantum dot enhanced solar cell (QDSC) short-circuit current over a baseline device and to improve power conversion efficiency of a QDSC compared to a device without strain compensation [52]. Figure 3.4 shows a comparison of an InAs QD stack in a GaAs host with and without strain compensation. On the left of figure 3.4, a strained QD superlattice stack is shown, with non-uniformity in the individual layers and some visible threading dislocations shown near the upper left corner of the image. These types of dislocations arise due to the strain from InAs growth on GaAs. To the right of the figure, a similar stack of QDs is shown with a GaP strain compensation layer. This stack shows more uniformity in the QD layers, compared with the uncompensated stack on the left and did not exhibit any threading dislocations.

Figure 3.4: Transmission electron micrographs of an InAs QD stack with no strain compensation (left) and GaP strain compensation (right).

The OMVPE process flow for SK grown InAs QDs in a GaAs host is shown schematically in figure 3.5 as a temperature and flow versus time plot. Figure 3.5 shows the initial GaAs buffer layer growth at high temperature, corresponding to the leftmost
stage on the bottom. At the second stage shown, the temperature is ramped down to facilitate the growth of the InAs QD layer followed by a LT GaAs layer. The temperature is then ramped up for HT GaAs growth and a HT GaP strain compensation layer, followed by another HT GaAs buffer layer. This process is then repeated until the desired number of QD layers is grown, when the temperature is ramped down under AsH$_3$ ambient.

Figure 3.5: Process flow for the OMVPE growth of InAs QDs in a GaAs host.
3.2 MATERIALS RESULTS

Test structures grown for materials characterization consisted of a 300nm thick n-type GaAs buffer layer grown at 620°C followed by a 5-period superlattice with repeating InAs QDs, GaP strain compensation layer and GaAs spacer layers as previously discussed. The InAs QDs were grown at 470° with differing coverage, $V/III$ ratio or growth rate as will be specified for each successive experiment. A 60s growth rate interrupt (GRI) was used to facilitate nucleation of InAs and formation of QDs. A 2.1nm thick low temperature GaAs cap was grown at the same temperature as the QDs to cap them and then temperature was ramped up to 585°C for growth of GaAs spacer layers and GaP strain compensation layers. The nominal thickness of the GaP layer was 4ML, based on the work of Bailey et al. as previously mentioned. The entire 5-period superlattice was capped with 30nm of GaAs as a buffer and a final uncapped layer of InAs QDs was grown on the surface for AFM analysis. A schematic cross-section of this structure is presented in figure 3.6 indicating the layers and thicknesses described.
3.2.1 Substrate Misorientation

Substrate misorientation, or the use of *vicinal* substrates is a technique commonly used in the manufacturing of *III-V* material solar cells. For triple junction solar cells (Ge bottom cell, GaAs middle cell and InGaP top cell) substrate misorientation is used to control the surface morphology of the InGaP top cell as well as to reduce the formation of anti-phase domains which occur as a result of a polarity mismatch between GaAs on Ge [53, 54]. Substrate misorientation results in the formation of atomically flat terraces with monatomic steps, whose width can be predicted by geometry as the tangent of the offcut angle with respect to the normal. A schematic of a misoriented substrate is given in figure 3.7, indicating the atomic steps, growth terraces and offcut angle, $\theta_{\text{vic}}$ with respect to the (001) surface normal.

During growth on vicinal surfaces, a phenomenon known as step bunching occurs for offcut angles greater than $\sim 0.5^\circ$, resulting from the overgrowth of material on
the substrate leading to growth terraces wider than geometrically predicted [55, 56]. Figure 3.8 shows AFM micrographs of three samples of (100) GaAs substrates misoriented 0° (left), 2° (center) and 6° (right) toward the (110) plane and one misoriented 2° toward the (111) plane. Table 3.1 gives the measured terrace widths for these samples as well as the geometrically predicted terrace widths. The 370nm terrace widths shown for the 0° offcut sample in table 3.1 are the result of very slight offcut for this sample. The 0° misorientation is a nominal value and the sample can actually be slightly offcut in reality. The figure shows that the width of the growth terraces decreased with increasing offcut angle while the density of terraces increased. Additionally, the terrace widths for the (111) misoriented sample are narrower than those of the 2° (110)
sample.

Figure 3.8: (100) GaAs substrates on-axis (left), misoriented 2° toward (110) (center) and 6° toward (110) (right).

Table 3.1: Geometrically predicted and experimentally measured terrace widths for varying degrees of offcut.

<table>
<thead>
<tr>
<th>Offcut</th>
<th>Terrace Width (nm)</th>
<th>Step Height (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>N/A 16.0 5.3 16.0</td>
<td>0.0 1.0 1.0 1.0</td>
</tr>
<tr>
<td>Experimental</td>
<td>370 81 47 51</td>
<td>2.0 6.3 3.6 5.7</td>
</tr>
</tbody>
</table>

The weakness of the geometrical prediction is that it makes the assumption that the step height is monatomic and that the formation of terraces is homogeneous. Terrace width predicted by geometry follows from trigonometry according to the equation

\[ l = \frac{h}{\tan(\theta_{\text{vic}})} \]  

(3.2)
where $l$ is the predicted terrace width, $h$ is the step height, which is taken to be $1ML$ and $\theta_{\text{vic}}$ is the nominal misorientation angle. In real application, however, offcut angles are nominal and there can be variance $\theta_{\text{vic}}$. Also, step flow growth of material on a vicinal surface tends to be accelerated an one direction while it is delayed in the opposite direction, which results in inhomogeneity of terrace widths, or step bunching in the presence of an Ehrlich-Schwoebel energy barrier [57].

### 3.2.2 InAs Coverage

To study the effect of varying InAs coverage on the formation of QDs, three sets of samples were grown on (100) GaAs substrates offcut $0^\circ$, $2^\circ$ and $6^\circ$ toward the (110) plane with InAs coverage ranging from $1.5ML$ to $2.2ML$ per QD layer in $0.2ML$ increments. Figure 3.9 shows $1 \times 1 \mu m$ AFM micrographs for this experiment. Shown in the figure, QDs tended to form along the step edges. This result is likely due to the energy barrier at a step kink which prohibits adatom nucleation across a step edge [58–60]. This behavior is predicted by the terrace ledge kink (TLK) model for crystal growth and surface diffusion. The model predicts that the energy required to remove a surface atom is related to the number of bonds to its nearest neighbors, second nearest neighbors and third nearest neighbors [47]. For an adatom, the total number of first, second and third nearest neighbors is 9, compared with that for a step atom and a kink atom, having a total of 12 and 13 atoms, respectively. An important conclusion of the observed phenomenon is that terrace formation as a result of substrate misorientation can be an effective tool for patterning the surface for QD growth.
Additionally, seen in figure 3.9, QD formation began to occur just before 1.8\textit{ML} InAs coverage for the 0° offcut sample, compared with 1.9\textit{ML} and 2.0\textit{ML} for the 2° and 6° samples, respectively. This indicates that the critical thickness, $\theta_c$, increased with increasing offcut. The suppression of QD formation at higher substrate misorientation angle is coupled with the suppression of QD ripening, whereby larger 3-D islands grow at the expense of smaller, coherent QDs through mass transport. This is shown in figure 3.10 which displays QD diameter plotted as histograms and indicates a decreased number of coalesced QDs with diameters in the 20-50\textit{nm} range for the 6° sample at 2.2\textit{ML}. This result can be attributed to the increased step edge density, mentioned previously, as well as the narrower terrace widths, shown in the figures by
the dashed lines. The step edges not only present an energy barrier for adatom diffusion as mentioned, but the smaller terrace widths reduce the reservoir of available indium adatoms for QD ripening [61]. Suppression of QD ripening is critical for improving device performance because coalesced QDs tend to be non-radiative centers and affect superlattice periodicity and overall strain balancing condition [51].

Figure 3.10: QD diameter histograms for different offcut substrates and InAs coverages.

Statistical properties of the QDs including average height, diameter and number density are presented in table 3.2. As shown in the table, the number density of the QDs increased with increasing InAs coverage for each of the three offcuts, with a lower "switch on" point for lower offcut angles, indicating a decrease in $\theta_c$. For coverages below $\theta_c$, a dash has been input in the table, indicating a density below a single QD per square micron, or a number density less than $1 \times 10^8 cm^{-2}$. Average QD height and diameter tended to increase with increasing InAs coverage for each offcut angle as expected, with the exception of the decrease in average diameter between 1.9 ML and 2.0 ML for the 0° samples. This can be attributed to the onset of QD ripening, shown in figure 3.9, whereby mass transport caused the migration of InAs from QDs
in the coherent mode to the coalesced QDs. A decrease in QD diameter for similar InAs coverage and increasing substrate misorientation angle was observed which was likely due to the decrease in terrace width as misorientation angle increased, as was illustrated in figure 3.10.

<table>
<thead>
<tr>
<th>InAs Coverage</th>
<th>Average QD Height (nm)</th>
<th>Average QD Diameter (nm)</th>
<th>Number Density ($10^{10} \text{cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5ML</td>
<td>N/A N/A N/A</td>
<td>N/A N/A N/A</td>
<td>– N/A N/A</td>
</tr>
<tr>
<td>1.7ML</td>
<td>1.8 N/A N/A</td>
<td>16 N/A N/A</td>
<td>0.20 – – –</td>
</tr>
<tr>
<td>1.9ML</td>
<td>2.0 1.7 1.6</td>
<td>20 15 14</td>
<td>2.03 2.10 0.19</td>
</tr>
<tr>
<td>2.0ML</td>
<td>2.3 2.0 1.8</td>
<td>19 16 15</td>
<td>4.84 3.36 2.27</td>
</tr>
<tr>
<td>2.2ML</td>
<td>N/A 2.3 2.0</td>
<td>N/A 17 16</td>
<td>N/A 6.73 5.40</td>
</tr>
</tbody>
</table>

Photoluminescence (PL) spectra were taken in order to measure the change in optical properties of the QDs grown on different degrees of offcut substrates. PL plots for each of the samples shown in figure 3.9 are given in figure 3.11. The figure indicates the GaAs band-to-band emission at $870 \text{nm}$, WL emission at $\sim 930 \text{nm}$ and QD ground state emission at $\sim 1050 \text{nm}$. The PL plots indicate a blue-shifted QD ground state PL response with increasing substrate misorientation at $2.0 \text{ML}$ InAs coverage with $1055 \text{nm}$, $1048 \text{nm}$ and $1038 \text{nm}$ corresponding to $0^\circ$, $2^\circ$ and $6^\circ$ misorientation, respectively. The blue shift is directly correlated to the observed decrease in QD height and diameter and is consistent with a $1/L^2$ energy dependence, predicted by quantum mechanics for a 3-D confining potential.

PL spectra for the $0^\circ$ misoriented samples showed no QD response until InAs
coverage of $1.9\,ML$ with subsequent WL response red-shift until critical thickness is reached at $\sim 1.8\,ML$. A similar WL response red-shift was observed for the $2^\circ$ and $6^\circ$ samples, stabilizing at a wavelength corresponding to the critical thickness, $940\,nm$ ($2^\circ$) and $930\,nm$ ($6^\circ$). This is an important result which illustrates the 2D to 3D transition during SK growth, whereby the WL increases in thickness until $\theta_c$ is reached, then any additional material incorporates directly into the 3D QD islands instead of the 2D WL. For the $2^\circ$ misoriented samples, QD response was first observed at $1.9\,ML$ coverage and for the $6^\circ$ samples, QD response was first observed at $2.0\,ML$ coverage. This onset of QD PL response at higher InAs coverage for increased substrate misorientation
strengthens the claim that critical thickness for QD formation increased as substrate misorientation angle increased. Additionally, the 0° 1.9ML sample exhibited a double peak in the QD region while the 2.0ML sample exhibited a shorter wavelength shoulder at 1020nm. These indicate a possible excited QD state which was not able to be spectrally resolved for the 2° and 6° samples, possibly due to the narrower QD PL full width half max (FWHM) for the 0° samples. Table 3.3 gives center wavelength and FWHM for the PL spectra presented in figure 3.11. The measured data shown in the table indicates a narrower FWHM for 0° and 2° offcut samples, indicating the suppression of inhomogeneous broadening or a more uniform overall size distribution for the QDs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>QD PL Peak Wavelength (nm)</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0ML, 0°</td>
<td>1050</td>
<td>70</td>
</tr>
<tr>
<td>2.2ML, 2°</td>
<td>1075</td>
<td>80</td>
</tr>
<tr>
<td>2.2ML, 6°</td>
<td>1065</td>
<td>90</td>
</tr>
</tbody>
</table>

In addition to investigating the effect of degree of substrate misorientation on QD formation, two additional sets of QD samples were grown on (100) GaAs substrates misoriented 2° toward (110) and toward (111) planes in order to investigate the effect of misorientation direction on QD formation. with increasing InAs coverage ranging from 1.9ML to 2.2ML in 0.1ML increments at a V/III ratio of 43. Figure 3.12 shows the 1×1 μm AFM micrographs for the two series. The top row of images in the figure correspond to the (110) misorientation direction and the bottom row corresponds to the (111) misorientation direction with the (100) surface normal and (110) misorientation
direction vector indicated.

Figure 3.12: Atomic force micrographs for increased InAs deposition of 1.9ML, 2.0ML, 2.1ML and 2.2ML, shown left to right. (Top) growth on substrates miscut toward (110) and (bottom) substrates miscut toward (111).

Figure 3.12 shows fully formed growth terraces for both misorientation directions, with a 45° difference between step edge alignment for the (111) misoriented samples and the (110) misoriented samples. This is expected, given the 45° angle between the (110) and (111) direction vectors. The figure also shows, albeit qualitatively, is that some degree QD coalescence occurred at lower InAs coverage for samples misoriented toward (111) compared with (110) misorientation. This result indicates a possible increased surface energy for the (111) misoriented surface compared with that of the (110) misoriented surface. Thus, for energy minimization reasons, adatom-adatom interactions may have been preferential, facilitating the ripening process [62]. Figure 3.13 is a quantitative representation of the QD statistical properties extracted
from the AFM images in figure 3.12. The plots represent the average QD diameter versus InAs coverage (blue circles), average QD height versus InAs coverage (red circles) and QD areal number density versus InAs coverage (green stars). Figure 3.13 shows that while both misorientation directions led to number density saturation, the samples misoriented toward (111) saturated at a slightly higher overall QD number density, of $\sim 2.8 \times 10^{10} \text{cm}^{-2}$ compared with $\sim 2.3 \times 10^{10} \text{cm}^{-2}$ for the (110) misoriented samples. This can be attributed to a higher density of growth terraces acting as a higher number of nucleation sites for QD formation. It is also shown in figure 3.13 that while InAs coverage was increased for the (111) misoriented samples, the overall QD size decreased slightly. This is likely due to the concurrent QD ripening, during which, larger 3D islands formed at the expense of smaller islands [62].

Figure 3.13: Statistical results extracted from AFM using SPIP software.

Normalized photoluminescence plots for this experiment are presented in figure 3.14, illustrating GaAs band-to-band emission at 870nm, WL emission at $\sim 930nm$ and QD
ground-state transitions between 1050\textit{nm} and 1100\textit{nm}. The PL results indicate a redshift in the QD ground state peak wavelength as InAs coverage was increased for the (110) misoriented sample set. This result is correlated to increased QD size with increased InAs coverage. PL showed no appreciable wavelength shift with increasing InAs coverage for the (111) misoriented sample set, indicating that increased InAs deposition led to the preferential formation of coalesced 3D islands which are not optically active.

![Normalized PL response for InAs coverage experiment.](image)

Figure 3.14: Normalized PL response for InAs coverage experiment.

For the 1.9\textit{ML} (110) misoriented sample, a weak QD emission peak was observed at 1050\textit{nm}, indicating that the critical thickness for QD formation may not yet have been achieved. Addition deposition led to QD dominated PL signal as shown in the figure. Also shown in the figure is that for both (110) and (111) misorientation, as QD response redshifted, the WL response blue shifted from 950\textit{nm} to $\sim$ 930\textit{nm} corresponding to the 1.9\textit{ML} and 2.2\textit{ML} coverage respectively. This is due to the migration of InAs from the WL to the QD through mass transport and has been previously observed and
confirmed [63].

3.2.3 $V/III$ Ratio

$V/III$ ratio is a measure of the ratio of group $V$ element to group $III$ element in a $III-V$ compound material. $V/III$ ratio has been shown to be a key growth parameter for the realization of high densities of uniformly sized InAs QDs [64]. Increased $V/III$ ratio, i.e. higher AsH$_3$ flow rate, compared to TMIn flow rate, results in the increased abundance of As atoms at the GaAs surface which reduces the migration length for the In species. This has been shown to decrease QD density and reduce the regularity in QD shape [64]. For this thesis, two series of samples with increasing $V/III$ ratio in the InAs QD layers of $V/III = 12, 43$ and $171$ were grown on (100) GaAs substrates misoriented $2^\circ$ towards the (110) and (111) plane.

Figure 3.15 presents atomic force micrographs of the two series, indicating the (100) surface normal and (110) offcut direction vectors for reference. The figure shows that for both (110) (top row) and (111) (bottom row) misorientation, higher $V/III$ ratio resulted in increased QD coalescence with decreased QD number density. This is consistent with what has been previously seen in the literature [65, 66] and is due to the reduced migration length for the indium species in the presence of higher $AsH_3$ concentration. Furthermore, since the metastable phase is prolonged, the wetting layer is thicker before the adatom nucleation phase, giving rise to coalesced, non-coherent islands and lower densities [67].

Figure 3.16 shows the QD statistics extracted from the AFM images using SPIP
Figure 3.15: Atomic force micrographs for increased $V/III$ ratios of 12, 43 and 171, shown left to right. (Top) growth on substrates miscut toward (110) and (bottom) substrates miscut toward (111).

software. In the figure, average QD diameter versus $V/III$ ratio is represented by blue circles. Average QD height versus $V/III$ ratio is represented by red circles and QD number density versus $V/III$ ratio is represented by green stars. Similar to the results from the InAs coverage study shown in figure 3.13, figure 3.16 indicates that despite coalescence and decreased number density of QDs with increasing $V/III$ ratio, the samples misoriented toward (111) exhibit overall higher densities of QDs for comparable $V/III$ ratios when compared to samples misoriented toward (110). This could be the result of an increased step edge density providing additional nucleation sites for In adatoms during growth for the (111) samples.
Figure 3.16: Atomic force micrographs for increased $V/III$ ratios of 12, 43 and 171, shown left to right. (Top) growth on substrates miscut toward (110) and (bottom) substrates miscut toward (111).

Photoluminescence spectra for the $V/III$ ratio sample series are presented in figure 3.17, which indicates GaAs band-to-band transition at $870\,nm$, a weak WL response at $\sim 920\,nm$ and QD ground state transitions between $1050\,nm$ and $1100\,nm$. The relative weakness of the WL transition illustrates the tradeoff between QD luminescence and WL luminescence. The wetting layer transition rate (intensity ratio between WL and QD) is reduced as the QD signal increases, due to geminate carrier capture into the lower energy QD ground state and the subsequent radiative carrier recombination. The figure shows a redshifted ground state QD emission peak with increasing $V/III$ ratio for both offcuts, corresponding to the similar increase in QD size as measured by AFM. For the (110) misoriented samples, the QD PL signal intensity for the $V/III = 171$ and 43 samples remained comparable to that of the $V/III = 12$ sample. This is a surprising result, given the fourfold decrease in QD number density spanning the sample set. More interestingly, the (111) misoriented samples exhibited
a continuous increase in QD PL signal intensity with increasing $V/III$ ratio. Such a result has not previously been published. Given the decrease in coherent QD number density and the increased presence of ripened, non-radiative QDs at $V/III = 171$, it was expected that the PL signal would decrease, since PL intensity is related to QD number density. The observed trends possibly indicate that the reduction in QD number density resulted in the overall decrease in strain-related defects which would otherwise act as non-radiative recombination centers.

![Figure 3.17: Photoluminescence spectra for samples in the $V/III$ ratio study.](image)

### 3.2.4 Growth Rate

In OMVPE, epitaxy is carried out in either a diffusion limited or reaction rate limited regime based on the temperature in the reaction chamber. At low growth temperatures, the reaction rate limits growth rate due to slower cracking of the precursor molecules. At high growth temperatures, the reaction rate is fast so the growth rate
becomes diffusion limited, or limited by the rate of mass transport to the wafer surface. Typical OMVPE growth occurs in the diffusion limited regime and in the case of a $V/III$ ratio greater than unity, the molar flow of the group $III$ precursor also limits the growth rate. As mentioned in chapter 1, QD growth occurs at temperatures far below those used for high quality GaAs growth ($470\degree C$ compared with $650\degree C$), thus the growth rate for InAs QDs is likely both diffusion limited as well as kinetically limited due to reaction rate. For this experiment, two series of QD samples were grown on (100) GaAs substrates misoriented $2\degree$ toward (110) and (111) planes with InAs growth rates of $0.1ML/s$, $0.2ML/s$ and $0.4ML/s$, controlled predominantly by the indium flow. Figure 3.18 shows $1 \times 1 \mu m$ atomic force micrographs of the two sample sets, indicating the (100) surface normal and (110) misorientation direction vectors. The figure shows that for both (110) and (111) misorientation, increased growth rate led to the suppression of QD coalescence. This could indicate that for a slower growth rate, adatom nucleation was preferentially carried out by the ripening process, possibly due to the increased nucleation time.

QD statistics extracted from AFM for these samples are shown in figure 3.19, indicating average QD height versus growth rate (red circles), average QD diameter versus growth rate (blue circles) and QD number density versus growth rate (green stars) for both offcut directions (show, top row). The bottom row of figure 3.19 shows the average QD aspect ratio, defined as the ratio of QD height to radius, versus growth rate for the two offcut directions. The top row of figure shows that increasing growth rate led to an increase in QD size for the primary (coherent) mode of QDs for the $(110)$
misorientation, while the same increase in growth rate led to a decrease in overall QD size for misorientation toward (111) with the most dramatic decrease being in the diameter of the QDs. The cause of this is likely due to the narrower terrace widths observed for the (111) misoriented substrates, as mentioned earlier in this chapter. Also shown in the top row of figure 3.19, the (110) misoriented samples exhibited a decrease in QD number density with increased growth rate while the (111) misoriented samples exhibited a fairly consistent number density of QDs with varying growth rate, averaging $\sim 8.5 \times 10^{10} cm^{-2}$. So far, it has been observed that (111) misoriented substrates resulted in higher QD number densities compared with similarly grown QDs on
(110) misoriented substrates, again, likely attributed to the narrower terrace width and subsequent increased step edge density as seen in table 3.1.

The bottom row of figure 3.19 shows that the QD aspect ratio decreased with increasing growth rate for the (110) misorientation while it increased for the (111) case. This is again related to the narrower terrace widths present on the (111) sample surface coupled with the greater In flow at higher growth rate which led to the preferential growth direction of the QDs to be vertical, rather than lateral. This is the opposite of
what was observed for the (110) misoriented samples, whose diameters remain large compared to their height and thus aspect ratio decreased with increasing growth rate.

Figure 3.20 shows normalized PL results for this experiment, indicating GaAs band-to-band transitions at $870\,nm$, WL response at $930\,nm$ and QD ground state transitions between $1050\,nm$ and $1100\,nm$. The PL results for the (111) misoriented samples indicated a blueshift in QD ground state transition with increasing growth rate. This can be explained by the increasing aspect ratio of the QDs resulting from smaller diameter with relatively similar height and the observed wavelength shift of $32\,nm$ which spans the sample set was predicted similarly by a quantum mechanical $k \cdot p$ simulation. $k \cdot p$ is a type of perturbation theory used for calculating band structure as well as optical properties of crystalline solids [68].

A large difference in the PL spectra between the (110) and (111) misoriented samples is that the QD ground state emission is high compared to the GaAs band-to-band

![Normalized photoluminescence data for increasing growth rate of 0.1ML/s, 0.2ML/s and 0.4ML/s.](image-url)
transition for the (110) samples, but is low compared to that observed for the (111) misoriented samples. This could possibly be the result of a reduced QD radiative lifetime for (111) misoriented samples compared with (110) misorientation. In order to further quantify this phenomenon, time resolved PL measurements should be performed.

3.3 SOLAR CELL RESULTS

In order to quantify the effects of QD inclusion in GaAs solar cells, a series of \( p-i-n \) structure solar cell devices were grown by OMVPE. Figure 3.21 shows, in cross section, the layer structure for a baseline GaAs \( p-i-n \) device with no QDs and a similar structure with QDs in the undoped or intrinsic region. The base of the devices consisted of \( 2 \mu m \) of Si-doped GaAs with a dopant density of \( 1 \times 10^{17} \text{cm}^{-3} \). The 10-period QD superlattice was grown within the \( 100nm \) intrinsic, or unintentionally doped region, with the same growth conditions as were investigated in the previous section. Baseline devices used as the control were grown with a \( 100nm \) thick \( i \)-region without a QD superlattice structure. The emitter consisted of \( 0.5 \mu m \) of Zn-doped GaAs with a dopant density of \( 1 \times 10^{18} \text{cm}^{-3} \). Two \( 50nm \) window layers of InGaP were grown at the front and back surface to reduce surface and interface recombination. A contact layer of heavily doped, \( p++ \) GaAs contact layer was grown to facilitate ohmic contact between the metal and semiconductor layers.

As-produced solar cell devices were fabricated using standard \( III-V \) processing and microlithographic techniques. Ohmic contacts were made to the \( p \) and \( n \)-type
regions using thermally evaporated Au/Zn/Au and Au/Ge/Ni/Au metallization, respectively. Each two-inch device wafer consisted of an array of seven $1 \times 1 \text{ cm}^2$ solar cells with grid finger shadowing of 4%, patterned by lithographic masks. Individual cells were isolated using wet chemical etch techniques. A representative, fully processed solar cell device wafer is presented in figure 3.22, indicating several $1 \times 1 \text{ cm}^2$ solar cell devices, $0.5 \times 1 \text{ cm}^2$ solar cells for concentration measurements and QE pads for spectral responsively measurement.

For solar cell testing, illuminated current-voltage characteristics were measured under one sun air-mass-zero (AM0) conditions using a TS Space Systems dual source solar simulator. The two lamps were calibrated using an InGaP$_2$ and GaAs solar cell provided by NASA Glenn Research Center. Spectral responsively measurements were performed using an OL Series 750 spectroradiometric measurement system with
standard lock-in technique.

A representative $AM0\ I - V$ curve is presented in figure 3.23 showing $I - V$ characteristics for a baseline device without QDs and the 1.9ML $0^\circ$ sample, 2.2ML $2^\circ$ sample and 2.2ML $6^\circ$ sample as indicated. The figure shows that for a ML coverage of 2.2, the $2^\circ$ sample (blue) exhibited an increase in $J_{sc}$ compared with the baseline sample (black). This increase in current occurred at the expense of the $V_{oc}$ which was reduced compared with the baseline. The cause for the $V_{oc}$ reduction is likely due to strain induced by the QD layers and has been observed for QD enhanced solar cells in literature [28,69]. Figure 3.24 gives the solar cell parameters ($J_{sc}$, $V_{oc}$, $FF$ and $\eta$) as a function of InAs coverage for each of the three substrate misorientations, $0^\circ$, $2^\circ$ and $6^\circ$.

As shown in figure 3.24, the 1.7ML and 2.2ML samples grown on $2^\circ$ misoriented
Figure 3.23: AM0 $I - V$ characteristics for a $1.9ML$ $0^\circ$, $2.2ML$ $2^\circ$ and $2.2ML$ $6^\circ$ misoriented toward (110) compared to a baseline device.

Substrates exhibited an increase of $0.01mA/cm^2$ and $0.25mA/cm^2$ in short-circuit current, respectively, compared to the baseline ($23.08mA/cm^2$ and $23.32mA/cm^2$ compared with $23.07mA/cm^2$ for baseline). $J_{sc}$ values for the $6^\circ$ samples, while not higher than the baseline value, exhibited an increase with increasing coverage after the formation of QDs at $1.9ML$. It is hypothesized that, for higher InAs coverages and appropriate strain balancing, the $6^\circ$ misoriented samples could perform with higher $J_{sc}$ compared to the baseline as a result of higher density of coherently strained QDs. Open-circuit voltage decreased with increasing InAs coverage for each of the misorientation angles. This result is typical for QD enhanced solar cell due to the narrowing of effective bandgap in the $i$-region by QD inclusion [70] and also due, possibly to
strain induced by the QD layers. The samples with higher InAs coverage exhibited the lowest $V_{oc}$ values of their respective series which can be attributed to the higher QD number density, as seen by AFM and shown in figure 3.9. It is important to note that for a coverage of 2.0ML, the 6° sample exhibited a slightly higher $V_{oc}$ than the 2° sample which is likely due to the decreased number of coalesced QDs for that sample, comparatively, as also shown in figure 3.9. Fill factor also tended to decrease with increased InAs coverage for all samples. The fill factor loss is linked to the reduction
in $V_{oc}$ due to a subsequent decrease in maximum power. Fill factor was also possibly degraded due to parasitic resistance which would also explain the $V_{oc}$ loss. Resulting from $V_{oc}$ and $FF$ loss, power conversion efficiency for these devices decreased with increasing InAs coverage, indicated in the bottom-right plot in figure 3.24. The $0^\circ$ samples exhibited the highest overall device efficiency and is attributed to the high relative $V_{oc}$ and $FF$, even despite the lower $J_{sc}$ compared to the $2^\circ$ and $6^\circ$ samples.

While a decrease in $V_{oc}$ is undesired and mitigation of such loss is desired, it is, to some degree, more important for the inclusion of a QD-enhanced middle junction of a TJSC that the current output be increased since an increase in current from the current-limiting cell (GaAs in this case) will result in an increase in overall device current and thus, lead to higher efficiency. The results in figure 3.24 show that devices grown on misoriented substrates led to higher $J_{sc}$ than for devices grown on on-axis substrates.

To further quantify the effect that the inclusion of QDs had on solar cell devices, spectral response was measured. The results for these measurements are presented in figure 3.25, shown as external quantum efficiency. Figure 3.25 shows that each sample set exhibited sub-bandgap response, indicating current collection from the QD layers, which has been plotted on a logarithmic scale in the inset of each plot. From the insets, it can be seen that the $2.2ML$ samples for both $0^\circ$ and $2^\circ$ exhibited longer wavelength spectral response compared with the $2.2ML$ $6^\circ$ sample. This result is consistent with the AFM and PL results given by figures 3.9 and 3.11 which indicated a decreasing QD size for increasing offcut angle. At lower InAs coverages, only a
WL response was observed in the inset plots in figure 3.25, for example, the $1.7ML\ 2^\circ$ sample. Longer wavelength response was observed as InAs coverage increased, indicating the thickening of the WL and eventual formation of QDs with increasing InAs coverage.

Figure 3.25: External quantum efficiency spectra for devices grown on substrates misoriented $0^\circ$, $2^\circ$ and $6^\circ$ toward (110).

It can also be seen in figure 3.25 that the baseline $2^\circ$ and $6^\circ$ devices with no QDs exhibited a slightly higher response in the wavelength region $\sim 450nm – 550nm$. This
response is associated with the emitter region of the solar cell device and thus, degradation in spectral response in this wavelength region can be explained by QD related emitter degradation, possibly due to strain effects. Devices grown on $0^\circ$ misoriented substrates with $2.0ML$ and $2.2ML$ InAs coverage showed EQE degradation near the band-edge compared with the $1.9ML$ sample. This wavelength region is associated with the base region of the solar cell device. Degradation of response in this region possibly indicates a loss in carrier capture through the space charge region of the cell due to recombination in the QD states. In order to further characterize this, voltage biased spectral response is required. By reverse biasing the solar cell, the electric field within the cell can be changed in order to facilitate increased carrier capture. If the degradation in EQE is removed under voltage bias, then it is clear that the observed degradation is related to the space charge region. Due to time constraints, this was not possible for this work and thus, this remains a hypothesis at this point.

Integrating the EQE spectrum with reference to the $AM0$ spectrum yields the short-circuit current as shown by equation 2.6 and table 3.4 shows integrated $J_{sc}$ values for the solar cells measured as well as measured $J_{sc}$ from $AM0$ light $I-V$. The measured $J_{sc}$ values tend to be lower than integrated values which is the result of the spectral mismatch of the lamps when simulating the $AM0$ spectrum. As was explained in chapter 2, integrated quantum efficiency provides a $J_{sc}$ calculation which does not take into account this mismatch and is thus an indicator of material quality, not of the measurement apparatus. Sub-880nm integrated $EQE$ indicates the contribution to $J_{sc}$ from the QD layers only. The table indicates that in general, QD contribution
was directly proportional to InAs coverage as expected. For a ML coverage of 2.0 and misorientation of 6°, the QD contribution to $J_{sc}$ was slightly reduced compared with the 1.9ML sample ($0.27mA/cm^2$ compared with $0.28mA/cm^2$) with an overall increase in both measured and integrated total $J_{sc}$. This indicates that the bulk material may have been slightly degraded for the 2.0ML sample compared with the 1.9ML sample due to shunting.

Table 3.4: Measured and integrated $J_{sc}$ values for 0°, 2° and 6° solar cell devices.

<table>
<thead>
<tr>
<th>InAs Coverage</th>
<th>AM0 $J_{sc}$ (mA/cm²)</th>
<th>Integrated $J_{sc}$ (mA/cm²)</th>
<th>Sub-880nm $J_{sc}$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0° 2° 6°</td>
<td>0° 2° 6°</td>
<td>0° 2° 6°</td>
</tr>
<tr>
<td>Baseline</td>
<td>– 23.07 22.68</td>
<td>– – –</td>
<td>– 0.09 0.09</td>
</tr>
<tr>
<td>1.7ML</td>
<td>– 23.16 22.18</td>
<td>– 23.76 23.76</td>
<td>– 0.22 0.22</td>
</tr>
<tr>
<td>1.9ML</td>
<td>22.36 23.08 22.07</td>
<td>23.83 23.74 23.39</td>
<td>0.26 0.28 0.28</td>
</tr>
<tr>
<td>2.0ML</td>
<td>21.73 23.02 22.16</td>
<td>23.21 23.74 23.47</td>
<td>0.25 0.27 0.27</td>
</tr>
<tr>
<td>2.2ML</td>
<td>21.89 23.32 22.32</td>
<td>23.45 23.51 23.36</td>
<td>0.27 0.36 0.31</td>
</tr>
</tbody>
</table>

Figure 3.26 shows graphically, the result of the QD contribution to the short-circuit current for each of these sample sets as a function of InAs coverage. The plot indicates that for each degree of substrate misorientation, the contribution to $J_{sc}$ increased with increasing InAs coverage with 2° demonstrating the greatest increase with coverage. This result is consistent with the one-sun AM0 results shown in figure 3.24 with the 2° 1.7ML and 2.2ML samples exhibiting increased $J_{sc}$ compared with a baseline device. Linear fits of the the data presented in figure 3.26 were performed and the results for each 2.2ML sample are shown in table 3.5. The fits indicate that over a narrow range of InAs coverage, the increase in sub-bandgap current collection is fairly linear. The slope for the 0° fit is roughly an order of magnitude smaller than that for the 2° and
$6^\circ$ samples. This indicates that for increasing InAs coverage, the QD contribution to $J_{sc}$ for the $0^\circ$ samples is not as pronounced and is likely due to a lower QD number density as seen by AFM.

![Figure 3.26: Integrated sub-bandgap $J_{sc}$ contribution for devices grown on substrates misoriented $0^\circ$, $2^\circ$ and $6^\circ$ toward (110).](image_url)
Table 3.5: Integrated Sub-bandgap \( J_{sc} \) for (110) Misoriented Substrate Devices

<table>
<thead>
<tr>
<th>Substrate Misorientation</th>
<th>Fit Line Slope ( (mA/cm^2/ML) )</th>
<th>QD ( J_{sc} ) contribution at 2.2ML ( (mA/cm^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0^\circ(110) )</td>
<td>0.04</td>
<td>0.27</td>
</tr>
<tr>
<td>( 2^\circ(110) )</td>
<td>0.28</td>
<td>0.36</td>
</tr>
<tr>
<td>( 6^\circ(110) )</td>
<td>0.19</td>
<td>0.31</td>
</tr>
</tbody>
</table>

For comparison of devices grown on (110) and (111) misoriented substrates, two sets of QD solar cell devices with InAs thickness of 2.0ML and 2.2ML were grown on (100) GaAs substrates misoriented 6° toward each direction. Due to reactor downtime and time constraints, devices on 0° and 2° misoriented substrates were not able to be grown. Figure 3.27 shows representative \( I-V \) characteristics for a baseline device as well as for the QD devices grown on both offcuts.

Also, due to the smaller number of data points available, an averaging of the performance of seven \( 1 \times 1 \) cm devices on each two-inch wafer was performed. One-sun \( AM0 \) results for this series are presented in figure 3.28 as box plots.

The figure shows that misorientation toward (111) resulted in a lower average \( J_{sc} \) compared to similar devices grown on substrates misoriented toward (110). However, for each offcut direction, \( J_{sc} \) increased with increased InAs coverage. This result is consistent with the results shown in figure 3.24 which showed increased current at higher InAs coverages for the 2° samples. Devices grown on (111) misoriented substrates performed, on average, with higher \( V_{oc}, FF \) and ultimately, efficiency. In order to further characterize the solar cell devices, spectral response measurements were performed and the results are presented in figure 3.29, displayed as external quantum
Figure 3.27: AM0 $I - V$ characteristics for a 2.0$ML$ and 2.2$ML$ (110) misoriented solar cell (red), and a 2.0$ML$ and 2.2$ML$ (111) misoriented solar cell (blue) compared with a baseline device (black).

Both sample sets exhibited sub-bandgap response which is shown enlarged on a logarithmic scale in the inset of each plot. Evident from the insets is that higher InAs coverage resulted in longer wavelength response. For 2.0$ML$ samples, only WL response was observed at $\sim 940nm$ with QD response observed for both 2.2$ML$ samples at longer wavelength. This result is consistent with the observed suppression of QD formation on 6° misoriented substrates. Additionally, (110) misoriented samples exhibited longer wavelength QD spectral response compared with (111) samples. This result was expected based on the larger QDs measured by AFM for (110) misorientation, comparatively. Also shown in figure 3.29, the (111) misoriented samples showed
some EQE degradation near the band edge compared to the baseline which could possibly be attributed to lower space charge region (SCR) response. This degradation, coupled with the reduced QD response for (111) misoriented samples compared to the (110) samples can possibly explain the lower measured $J_{sc}$ shown in figure 3.28. Integrating the sub-bandgap EQE response to determine the $J_{sc}$ response due to the
QDs resulted in lower $J_{sc}$ contribution from samples grown on (111) misoriented substrates. Results of this are presented in table 3.6, which verifies that the (111) samples exhibited lower $J_{sc}$. The greater contribution to $J_{sc}$ from the QDs coupled with the higher spectral response near the GaAs band edge resulted in higher overall $J_{sc}$ for the (110) misoriented sample which is consistent with what was measured under AM0. For inclusion in a TJSC device, the current through the (111) misoriented device should be enhanced, although given the higher $V_{oc}$ and ultimately, higher efficiency, a TJSC grown on a substrate misoriented toward (111) could exhibit enhanced overall efficiency.

Table 3.6: Integrated Sub-bandgap $J_{sc}$ for (110) and (111) Misoriented Substrate Devices

<table>
<thead>
<tr>
<th>InAs Coverage</th>
<th>6° (110) Sub-bandgap $J_{sc}$ ($mA/cm^2$)</th>
<th>6° (111) Sub-bandgap $J_{sc}$ ($mA/cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>2.0ML</td>
<td>0.27</td>
<td>0.21</td>
</tr>
<tr>
<td>2.2ML</td>
<td>0.31</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Chapter 4

Quantum Dot growth in a Large-Area Commercial OMVPE Reactor

4.1 MOTIVATION

In chapter 3 InAs QD growth has been investigated and characterized for 2” substrates, however, these small area substrates are primarily research-lab samples and the PV industry is moving toward larger area substrates such as 4” and 6” wafers [71]. Naturally, for larger area wafers, larger area reactors are needed to grow samples in high volume. This can potentially present challenges for OMVPE growth of uniform QDs since the pyrolysis reactions and subsequent diffusion of material is driven by thermodynamics and larger area reaction chambers can have different temperature and flow profiles. For this chapter of this work, InAs QD samples grown on 4” GaAs substrates in a 400mm commercial reactor (shown, figure 4.1) were investigated and characterized.

The first goal of this part of the work was to be able to control the OMVPE growth
process in order to grow uniform QDs across the entire susceptor of the reactor shown in figure 4.1. AFM and PL measurements were used to characterize QD growth in terms of QD size and number density and subsequent results will be presented in this chapter. The second goal focused on the inclusion of QDs into commercially available dual and triple junction solar cells for improved device current and overall power conversion efficiency enhancement. \textit{AM0} performance as well as spectral responsivity results will also be presented in this chapter.

4.2 EXPERIMENTAL SET-UP

The samples measured in this study were InAs QD test structures grown on 4” GaAs substrates with varying number of buried QD layers ranging from 1x to 20x samples for PL measurements and a single uncapped QD layer for AFM measurements. A series of $1 \times 1 \text{cm}^2$ double junction and triple junction solar cell devices were also grown with QDs based on the test structure growth parameters for \textit{AM0} testing. A cross-section
of each type of sample is given in figure 4.2. Note that for a double junction device, the InGaP top cell and top tunnel junction are not present.

Figure 4.2: (a) Cross-section of a QD test structure showing buried QDs for PL and surface QDs for AFM. (b) TJSC device stack with QD superlattice grown in the i-region of the (In)GaAs junction.

Similar to the 2” QD samples investigated in the previous chapter, material and statistical properties of QDs grown on 4” wafers were characterized using AFM and PL. Triple junction solar cell device characterization was performed using the TS Space Systems two-source solar simulator shown in figure 2.7. EQE measurements were performed using the Optronics Laboratories OL750 monochromator shown in figure 2.10, but modified in order to make individual junction SR measurements.

The SR setup was augmented with LED pucks illuminated at a specific wavelength used to saturate each junction not being measured so that the measured SR is coming only from the junction being tested. The working principle behind this technique as explained in chapter 1 during the discussion of triple junction solar cell operation, is that the three solar cell junctions are connected in series, thus the net current produced
by the device is limited by the junction with the smallest current. With the non-working junctions saturated with current, the junction being measured certainly outputs the lowest current and thus the spectral response is known to come only from that junction. A picture of an LED puck used as well as the modified SR setup is given in figure 4.3.

Figure 4.3: LED puck used to bias nonworking junctions for EQE measurements of QD enhanced TJSC devices.

### 4.3 MATERIAL RESULTS

Preliminary attempts at the OMVPE growth of InAs QDs on 4” GaAs substrates in the large-area reactor are shown as $1 \times 1 \mu m^2$ AFM micrographs in figure 4.4 (left). The figure shows that islands of InAs formed on the surface, but with no real degree of regularity in size and shape. The surface looks lumpy instead of smooth, showing no atomic terraces which were seen in AFM images in chapter 3. Furthermore, figure 4.4 (right) shows the PL spectrum of this sample. Only a weak GaAs emission peak was observed at $870 nm$, with no discernible QD-related emission at longer wavelengths.
Based on the AFM in figure 4.4, it is clear that InAs was deposited on the surface, but that in order to realize stronger QD response in the 1100 nm region, growth parameters needed to be adjusted. The next step taken to optimize the QD growth was to adjust the alkyl settings in the reactor to improve the QD size and shape uniformity. By adjusting the flow rates through each of the alkyl jets in the reactor, of which there were four, the flow profile in the reactor can be changed. Thus, the distribution of available material for epitaxial growth can be adjusted so that the material deposits in a more desired way. Two samples were selected for this study. Sample A was grown with increased TMIn flow toward the outer part of the reactor shown in figure 4.1 with decreased flow toward the inner part and sample B had increased TMIn flow towards the inner part of the reactor with decreased flow toward the outer part. A V/III ratio of 12 was used and QDs were grown at 450°C. Figure 4.5 shows the AFM results from
Compared with figure 4.4, the QD size and shape were better controlled, with very distinct InAs QDs formed along terrace edges as previously seen in chapter 3 for the 2” samples grown at NASA. Table 4.1 gives the AFM statistics for these samples extracted using SPIP. As shown, both samples exhibited a fairly consistent QD size with less than 2nm difference in average diameter and almost identical average height. The number density was slightly reduced for sample B, but given that the samples both presented relatively low number densities, the values reported are statistically similar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average QD Height (nm)</th>
<th>Average Diameter (nm)</th>
<th>Number Density ($\times 10^{10}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.1</td>
<td>25.5</td>
<td>0.58</td>
</tr>
<tr>
<td>B</td>
<td>3.2</td>
<td>23.9</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 4.1: AFM statistics extracted using SPIP for improved alkyl samples

PL results for these samples are given in figure 4.6 indicating GaAs band-to-band
transitions at 870\textit{nm}, WL transition at 950\textit{nm} and QD ground state transition at \(\sim 1000\textit{nm}\). The PL results show that sample B exhibited a brighter QD response at 1020\textit{nm} compared with sample A. This is directly attributed to the higher QD number density for sample B compared with sample A as seen in the AFM images in figure 4.5.

![Figure 4.6: PL Results for samples with improved alkyl settings.](image)

The goal of achieving an intermediate band solar cell (IBSC) involves the growth of highly coherent and optically coupled QDs to form an intermediate band acting as a metastable state for charge carriers to be promoted into the conduction band. To do this, the WL response must be suppressed and the QDs must be more optically active. Thus, further improvement of QD growth was desired. In an attempt to increase the
PL response from the QDs by increasing their number density, a series of samples was grown with varied InAs deposition time similar to that investigated in chapter 3. Two samples were selected for study which were grown with $20\,s$ and $22.5\,s$ of InAs deposition time. Figure 4.7 shows the AFM results from this experiment.

![AFM micrographs of QD growths](image)

Figure 4.7: $1 \times 1\,\mu m^2$ AFM micrographs of QD growths in the large reactor with increased InAs Deposition time. Sample A (left) 20s deposition time and sample B (right) 22.5s deposition time.

Figure 4.7 shows that longer deposition time (sample B) led to an increased density of coalesced QDs. This result is similar to results shown in figure 3.12 for the 2" sample growths, which indicated that at long InAs deposition times, deposited material tends to nucleate preferentially to already formed islands rather than form new coherent QDs. Thus, shorter InAs deposition times were required to form coherent QDs. The AFM statistics for these two samples are given in table 4.2. Indicated in the table is that on average, the longer deposition time resulted in larger coherent QDs and a slightly higher number density of QDs. This was the expected result for this type of
experiment.

Photoluminescence results for these two samples are shown in figure 4.8 which indicates GaAs band-to-band transition at $870\text{nm}$, WL transition at $940\text{nm}$ and QD ground state transition past $1000\text{nm}$. A red-shift of $25\text{nm}$ was measured between the $20s$ and $22.5s$ QD ground state peaks. This is consistent with the size change measured by AFM in figure 4.7 and presented in table 4.2. Also, despite the red-shifted QD response, the WL response did not shift with increasing deposition time. This is consistent with what was discussed in chapter 3 regarding WL evolution. The WL continues to grow until $\theta_c$ and as soon as QD formation begins, the WL does not get thicker with increasing deposition. Figure 4.8 also shows an increase in the QD peak intensity for the $22.5s$ deposition sample compared with the $20s$ sample was observed. This is consistent with the increase in number density of QDs also reflected in the AFM and table.

The next experiment performed was to adjust the thickness of the GaAs spacer layer in order to modify the coupling between QD states. For this experiment, two samples were selected for study with different LT and HT GaAs spacer layers. The sample set consisted of a sample B, which twice the LT and HT GaAs thickness compared with sample A. AFM results are shown in figure 4.9.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average QD Height (nm)</th>
<th>Average Diameter (nm)</th>
<th>Number Density ($\times 10^{10}\text{cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.1</td>
<td>21.1</td>
<td>2.11</td>
</tr>
<tr>
<td>B</td>
<td>2.4</td>
<td>22.9</td>
<td>2.67</td>
</tr>
</tbody>
</table>
Figure 4.8: PL results for samples with varied InAs deposition time.

Qualitatively, there is not much difference in the size distributions of QDs from sample A to B, which isn’t a surprising result as they were grown with the same growth conditions. This is supported quantitatively by table 4.3. Sample B exhibited some QD coalescence, but this may not be statistically relevant given the low number of coalesced QDs. Sample A also exhibited a slightly higher number density of QDs compared with sample B. This could simply be an artifact of the region chosen for measure by AFM and does not represent an important statistical variance.

Figure 4.10 shows the PL results for these two samples, indicating a very weak relative GaAs band-to-band transition at 870\text{nm}, WL transition at 940\text{nm} and QD ground
Figure 4.9: $1 \times 1 \mu m^2$ AFM micrographs of 10x QD growths in the large reactor.

Table 4.3: AFM statistics extracted using SPIP for varied GaAs spacer layer samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average QD Height (nm)</th>
<th>Average Diameter (nm)</th>
<th>Number Density ($\times 10^{10} \text{cm}^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>2.1</td>
<td>22.4</td>
<td>2.86</td>
</tr>
<tr>
<td>B</td>
<td>2.1</td>
<td>21.1</td>
<td>2.65</td>
</tr>
</tbody>
</table>

state transition at $\sim 1000nm$. Shown in the PL spectra, sample B exhibited a much weaker ground state PL response compared with sample A. The WL transitions seem to have been dominant in the PL response for sample B, unlike what was observed for sample A, whose PL spectrum was QD dominant. The relative strength of the QD PL response for sample A compared with sample B may be due to stronger QD coupling, increasing PL efficiency, as a result of the thinner GaAs spacer layers. The wavelengths of the QD peaks are not appreciably wavelength shifted with respect to one another, indicating a similarity in QD size as measured by AFM.

It has now been demonstrated that the OMVPE growth process could be controlled
in a large-area reactor to produce relatively high densities of QDs with uniform size. In order to increase the QD density further without increased QD reactor pressure and temperature should be further optimized [72]. Nevertheless, with QD densities and size uniformities improved compared with preliminary results, the next goal was to investigate the effect of QD inclusion in the (In)GaAs junction of a double and triple junction solar cell device.
4.4 SOLAR CELL RESULTS

In order to characterize double junction solar cells (DJSC) and TJSCs, a series of solar cells were grown by the commercial vendor with QD layers grown at NASA GRC. The wafers supplied by the vendor were 4” templates with a series of 52 individual $1 \times 1 \text{cm}^2$ solar cell devices which were processed using standard $III - V$ processing techniques. Figure 4.11 shows a representative solar cell device wafer with individual solar cells which were used for testing removed by a dicing process. They are labeled 14, 21, 29, 36 and 42 as indicated in the figure.

Figure 4.11: Representative solar cell device wafer with $1 \times 1 \text{cm}^2$ solar cells arranged in a grid pattern.

4.4.1 Double Junction Solar Cell Results

Double junction (In)GaAs/Ge solar cell devices were grown and fabricated to analyze the performance of the (In)GaAs junction with and without the inclusion of 10 QD
layers prior to the addition of the InGaP top junction of the TJSC stack. The growth of
the DJSC was similar to the growth of the TJSC with the exclusion of the InGaP top
cell and tunnel junction. As indicated in figure 4.11, a series of five $1 \times 1 cm^2$ solar cell
devices was diced from the 4” wafer in order to test the performance of QD enhanced
DJSC devices across its entire diameter. Figure 4.12 shows the $I - V$ characteristics of
the QD enhanced DJSC devices across the wafer diameter compared with a baseline
device with no QDs. Shown in the inset of figure 4.12 are the extracted solar cell
device parameters, $J_{sc}$, $V_{oc}$, $FF$ and $\eta$. Note that in the figure, positions $F$, $FC$, $C$,
$AFC$ and $AF$ correspond to solar cell devices 14, 21, 29, 36 and 42 in figure 4.11,
respectively.

![Figure 4.12: $I - V$ characteristics for the five $1 \times 1 cm^2$ QD DJSC solar cell devices across a 4” wafer compared to a baseline. Inset table indicated solar cell device parameters extracted from the $I - V$ curves.](image)
The figure indicates an average decrease in $V_{oc}$ of 50mV for the QD devices compared with the baseline device. The QD enhanced devices do, however show an average increase of 1.0mA/cm² in $J_{sc}$ compared with the baseline, with a 1.1mA/cm² improvement for the QD cell which performed with the highest efficiency. The observed $V_{oc}$ decrease with subsequent $J_{sc}$ increase is consistent with results from single junction QD GaAs devices that outperformed baseline devices [73]. To further elucidate the effect of QD inclusion to the (In)GaP junction, spectral responsivity was measured for these devices. The results from spectral responsivity measurements are given in figure 4.13, shown as external quantum efficiency.

![Figure 4.13: External quantum efficiency of 10x QD DJSC devices compared to a baseline DJSC device. Electroluminescence spectra shown in green.](image)

The lefthand plot of figure 4.13 shows, primarily the bulk (In)GaAs junction response with the dotted vertical line indicating the GaAs band edge at 870nm. The
righthand plot is a zoomed-in view of the spectral responsivity past 880nm showing the sub GaAs bandgap response due to the QD layers. An electroluminescence spectrum for the QD sample is also shown on the righthand plot in green, indicating the response due to the QDs near 1000nm. Spectral response measurements indicated that the bulk material did not exhibit any degradation with the inclusion of the QD superlattice. Integrating the sub-bandgap response revealed a $J_{sc}$ contribution of $0.02mA/cm^2/QD$ layer which is similar to that of a 40 layer QD GaAs single junction device which outperformed the baseline device [73]. These results show that the inclusion of a QD superlattice can improve the current of a DJSC GaAs/Ge device compared to a baseline device. Based on the integrated $J_{sc}$ values, for the DJSC device to exceed baseline device efficiency, 45 QD layers should be added and adequately strain compensated. Nevertheless, the current enhancement proves a positive result for moving toward TJSC Devices. TJSC device performance will be discussed in the next section.

4.4.2 Triple Junction Solar Cell Results

Similar to the DJSC devices discussed in the previous section, triple junction devices were grown and fabricated. The device design consisted of a Ge substrate, Ge bottom cell, (In)GaAs middle cell and an InGaP top cell, each connected by tunnel junctions. Devices were fabricated on 4” wafers and for solar cell testing, a sampling of devices across the diameter of the wafer was used similar to figure 4.11. AM0 $I-V$ characteristics for the TJSC devices are presented in figure 4.14 with the inset table indicating solar cell device parameters extracted from the $I-V$ curves.
The $I-V$ curves for the QD enhanced samples shown in the plot indicate a high degree of uniformity, which indicates uniform QDs and adequate strain balancing across the 4” wafer despite QD number density differences. An average $V_{oc}$ reduction of 120mV was observed for the QD devices compared with the baseline device. This is compared with the 50mV reduction in $V_{oc}$ observed for the DJSC devices. Assuming similar performance for the (In)GaAs junction in both the DJSC and TJSC structures, the AM0 results indicate a 70mV reduction in $V_{oc}$ for the InGaP junction. This performance reduction compared with a baseline device indicates a possible degradation of material quality in the InGaP junction. InGaP material quality can be affected by the surface morphology and strain which can be changed or induced by the inclusion of...
QDs in the middle junction [74–76].

Spectral response measurements for the TJSC with and without QDs are presented for each junction in figure 4.15. The top plot represents the response for the InGaP cell only, the middle plot represents the response for only the (In)GaAs junction and the bottom plot represents the response for just the Ge bottom cell. The inset in the middle plot indicates the response beyond the band edge for GaAs and is shown on a logarithmic scale.

![Figure 4.15: EQE plots for each junction in the TJSC stack. (top) InGaP junction, (middle) (In)GaAs junction with 10x QD superlattice (inset) and (bottom) Ge junction.](image)

The EQE plots for each junction indicate a consistent response across the 4” wafer as well as similar response for QD samples compared with baseline samples with
increased response between 900nm and 1050nm for the middle junction due to the inclusion of the 10 layer QD superlattice. Integrated $J_{sc}$ values are given for each subcell in table 4.4. From the table, it is observed that the inclusion of a 10 layer QD superlattice generated 0.3mA/cm² increase in $J_{sc}$ compared with the baseline. The table also indicates that the top cell was current-limiting, thus, additional current from the QDs was not present in the $AM0 I−V$ plots shown in figure 4.14. In order to realize improved efficiency for the TJSC compared with the baseline, the top cell should be optimized to increase current output. This could possibly be achieved by improving the morphology of the QD layers beneath through variation of growth parameters like growth temperature or gas flow [72].

<table>
<thead>
<tr>
<th>Junction</th>
<th>Integrated $J_{sc}$ (mA/cm²) Baseline</th>
<th>10x QD</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaP</td>
<td>17.2</td>
<td>17.5</td>
</tr>
<tr>
<td>(In)GaAs</td>
<td>17.5</td>
<td>17.8</td>
</tr>
<tr>
<td>Ge</td>
<td>28.9</td>
<td>28.3</td>
</tr>
</tbody>
</table>
Chapter 5

Summary, Conclusions, & Future Work

5.1 QUANTUM DOT GROWTH ON 2” GaAs SUBSTRATES

5.1.1 Summary & Conclusions

InAs QDs have been grown by OMVPE on vicinal GaAs substrates and characterized by AFM and PL. In order to study the growth process, three series of samples were grown each investigating the effect of varying a single growth parameter. These experiments included varying InAs coverage, varying $V/III$ ratio and varying InAs growth rate. Additionally, the effect of substrate misorientation angle and direction was investigated by growth of QDs on (100) GaAs substrates misoriented toward either (110) or (111) crystal planes. Single junction GaAs $p-i-n$ solar cells were grown with QDs implanted in the $i$-region and characterized by one-sun illumination under a simulated AM0 spectrum and by spectral responsivity.

AFM results indicated that QD ripening can effectively be suppressed with increased misorientation angle in the vicinity of the (110) plane. Additionally, increased
misorientation angle demonstrated an increase in $\theta_c$ for QD formation which was evidenced by the later onset of QD formation for $6^\circ$ misorientation of $2.0ML$ compared with $1.9ML$ and $1.8ML$ for $2^\circ$ and $0^\circ$ misorientation, respectively. The cause for this was attributed to the higher density of narrower growth terraces formed at higher offcut angle, which reduced the reservoir of In adatoms for QD nucleation and subsequently, QD coalescence. PL results for increased InAs coverage indicated a WL peak red-shift for successive coverages below the critical InAs thickness for QD formation but revealed that as soon as QDs began to form, the WL thickness remained at a constant thickness. This is an important result indicating that at the 2D-3D transition of SK growth, additional InAs bonds preferentially to QDs rather than the WL due to increased compressive strain.

Results from AFM comparisons between $(110)$ and $(111)$ misorientation direction indicated that, on average, higher number densities of QDs tended to form on $(111)$ misoriented substrates compared with $(110)$ misorientation. AFM also that increased QD coalescence occurred at lower InAs coverages or in greater number for $(111)$ misorientation compared with that for QDs grown on $(110)$ misoriented substrates. Most notably, a QD number density averaging $\sim 8.5 \times 10^{10} cm^{-2}$ was observed for $(111)$ misoriented samples with varying growth rate, compared to the highest observed value of $5.9 \times 10^{10} cm^{-2}$ for the $(110)$ misoriented samples. Also, for an InAs coverage of $2.2ML$, a coalesced QD number density of $1.3 \times 10^{9} cm^{-2}$ was observed for the $(111)$ misoriented samples compared with the $0.2 \times 10^{9} cm^{-2}$ for similar InAs coverage on the $(110)$ misoriented sample. This increase in QD coalescence, on average, as well...
as the higher observed number densities of QDs for (111) misorientation can be attributed to a decrease in the Erlich-Schwoebel (ES) energy barrier for the nucleation of In adatoms. A higher ES barrier may have prevented such nucleation on (110) misoriented samples to some degree. PL data for the $V/III$ ratio study revealed an increase in QD ground state emission for increased $V/III$ ratio from $V/III = 12$ to $V/III = 171$, despite a fourfold decrease in QD number density from $\sim 8 \times 10^{10} cm^{-2}$ to $\sim 2 \times 10^{10} cm^2$ for both misorientation directions. This is an interesting result and could possibly indicate a higher quality crystalline material, although further studies into temperature dependent PL to extract QD activation energies could better quantify the cause for increased PL.

Solar cell AM0 results revealed that misorientation $2^\circ$ toward (110) resulted in increased $J_{sc}$ at higher coverage ($2.2 ML$ InAs) compared with a baseline device. Samples misoriented $6^\circ$, while not exhibiting increased current output over a baseline device, showed a consistent increase in current at InAs coverage exceeding $1.9 ML$. Due to the lower density of coherent QDs for $6^\circ$ samples compared with similar coverages on the $2^\circ$ misoriented samples, the decrease in current was expected, but it is expected that higher InAs coverage on $6^\circ$ misoriented samples would result in increased $J_{sc}$ compared to a baseline. Higher InAs coverage could be achieved with less QD ripening on $6^\circ$ misoriented substrates as shown by AFM. Solar cell results showed that $0^\circ$ misoriented samples exhibited the highest $V_{oc}$ and $FF$ values in the series which in turn, led to higher $\eta$ values. This result indicated that in order to improve power conversion efficiency, $V_{oc}$ loss observed in the misoriented substrate devices should
be mitigated, possibly by more careful control of QD morphology during growth. EQE results indicated that despite the lower efficiencies, the misoriented substrates (both $2^\circ$ and $6^\circ$) resulted in greater $J_{sc}$ contribution from the QD layers with $2^\circ$ exhibiting the most current gain from the QDs. This solidifies the claim that mitigation of $V_{oc}$ degradation would be a crucial factor in producing devices on a misoriented substrate which outperform the baseline device.

Devices grown on substrates misoriented toward (111) exhibited a reduction in $J_{sc}$ compared with those misoriented toward (110) and as well, the baseline device. Despite this global reduction in current, increasing InAs coverage from 2.0ML to 2.2ML resulted in a $J_{sc}$ enhancement of 0.2mA/cm$^2$ with virtually no reduction in $V_{oc}$. Thus, higher InAs coverage for samples misoriented toward (111) could improve the $J_{sc}$ to a value competitive with the baseline device. To do this, a careful balance of growth parameters such as growth temperature should be performed to mitigate the QD ripening process which was seen to greater effect for the (111) misoriented samples compared with the (110) misoriented samples by AFM. Improving $J_{sc}$ for the (111) misoriented samples is of interest because (111) misoriented devices performed with higher $V_{oc}$, $FF$ and $\eta$ on average, compared with the (110) misoriented samples. Substrate misorientation toward (110) has been extensively studied [77], but to date, little work has been published which fully characterizes QD enhanced GaAs solar cells on (100) GaAs substrates misoriented towards (111).
5.1.2 Future Work

In continuing with the work performed in this work on substrates misoriented toward (111), solar cell devices should be grown which reflect the changes to $V/III$ ratio and growth rate. Specifically, solar cell devices with $V/III = 171$ could prove interesting given the PL data collected for these samples and presented in chapter 3. The high PL signal from the QDs for the high $V/III$ ratio samples, despite increased QD coalescence and decreased QD number density makes the interesting case that, due to increased radiative recombination rate, $V_{oc}$ degradation can be minimized compared to a baseline device [78]. Furthermore, a control of growth parameters which would reduce the number of coalesced QDs could greatly improve solar cell performance since a reduction in coalesced QD number density would result in less variation in local strain balancing condition and thus minimize strain-related defects due to large QD islands.

As well, the growth of solar cell devices and test structures on substrates misoriented $0^\circ$, $2^\circ$ and $6^\circ$ toward (111) could help fully characterize QD growth on (111) misorientation by giving insight to the $\theta_c$ value as a function of offcut angle. AFM results for $2^\circ$ (111) samples indicate that (111) misorientation might result in a lower critical thickness for QD formation, but more samples are required to make this a quantitative claim. Additionally, based on current gains reported, with $2^\circ$ (110) misoriented samples proving higher $J_{sc}$ compared to the baseline sample, a set of samples with optimized QD growth conditions should be grown, varying the number of QD layers in the repeat superlattice to further improve not only current output, but overall efficiency.
Performance for a 40-layer InAs QD superlattice in a single junction GaAs solar cell has been reported to exceed that of a baseline device [73] which was previously unobserved. Thus, with careful balance of growth parameters to minimize QD coalescence as well as adequate strain balancing, high stacks of QDs can be integrated into solar cell devices which yield enough current enhancement to improve overall device efficiency. Given the promise of high relative $V_{oc}$ comparable with baseline samples (0.95$V - 1.00V$) [50] for the (111) misoriented substrate devices, the potential exists for high efficiency devices utilizing QD stacks upward of 20 layers.

5.2 QUANTUM DOT GROWTH IN A LARGE-AREA OMVPE REACTOR

5.2.1 Summary & Conclusions

InAs QDs have been grown on 4” GaAs substrates in a 400mm commercial reactor and characterized by AFM and PL spectroscopy at room temperature. Additionally, double junction and triple junction solar cell devices were grown, fabricated and characterized using one-sun $AM0 I - V$ characteristics and spectral responsivity. DJSC devices consisted of a Ge substrate, Ge bottom cell and (In)GaAs cell with and without QDs, and connected by a tunnel junction. TJSC devices consisted of the same layer structure as the DJSC devices with the addition of another tunnel junction and InGaP top cell. Each solar cell device structure was grown on a 4” wafer with a grid of 52 $1 \times 1cm^2$ solar cell devices fabricated using standard III–V processing techniques.
Preliminary attempts at uniform QD growth proved unsuccessful as AFM results showed no degree of uniformity of the observed surface features. The surface appeared to have InAs islands but they did not align along growth terraces as was the case for the 2” sample growths investigated in chapter 3. PL for the first growth revealed a very weak GaAs band-to-band peak at 870 nm but QD transitions were not able to be resolved from the noise, likely as a result of the high degree of coalescence of InAs islands. The next step taken was to reduce the alkyl flow through the injectors in the reactor chamber to improve QD nanostructures. AFM results showed that for reduced alkyl flow through the injector heads, a low density ($0.58 - 0.72 \times 10^{10} \text{cm}^{-2}$) of uniformly sized QDs could be grown, aligning along step edges with an average size of $\sim 3 \times 25 \text{nm}$ height and base, respectively. PL results for these samples indicated that for the higher density ($0.72 \times 10^{10} \text{cm}^{-2}$) sample, a QD ground state transition shoulder began to become visible at 1020 nm. This was a positive result, indicating that buried QDs were able to be grown and were optically active.

To increase the density of QDs and thus, the PL response, a series of samples were grown with longer InAs deposition times. For a deposition time of 20 s, a density of $2.11 \times 10^{10} \text{cm}^{-2}$ was observed for QDs with average size $2.1 \times 21.1 \text{nm}$. A second sample with a longer growth time of 22.5 s was grown, exhibiting a larger density of $2.7 \times 10^{10} \text{cm}^{-2}$ corresponding to slightly larger QDs. Both of these samples exhibited QD coalescence which was likely the result of long InAs deposition time. The 22.5 s sample exhibited a higher density of coalesced QDs ($0.23 \times 10^{10} \text{cm}^{-2}$ compared with $0.10 \times 10^{10} \text{cm}^{-2}$ for the 20 s sample) as expected. The effect of higher QD number
density was apparent in the PL spectra of these samples, indicating an increased QD ground state PL peak with respect to the WL transition peak and the $22.5s$ sample exhibiting an increased PL signal corresponding to the QD ground state transition.

The final step investigated was to examine the effect of GaAs spacer layer thickness on QD coupling by varying both low temperature (LT) and high temperature (HT) GaAs spacer layer thickness. A set of samples grown with a standard LT+HT thickness and a spacer with twice the LT and HT thickness were grown and investigated. As expected, the AFM showed little difference in the QD morphology and overall number density. This result was expected as the change was to the capping layer for the buried QDs and should not have affected the surface QDs. However, the QD uniformity remained good, showing almost no QD coalescence by AFM. PL results indicated that for a thinner spacer layer thickness, the QD ground state transition was over three times as strong as the thicker spacer layer sample. This indicated stronger QD state coupling and higher PL efficiency. This result was important in moving toward inclusion of QDs in DJSC and TJSC stacks as it was demonstrated that uniform QDs could be grown which displayed strong optical characteristics.

DJSC devices were grown and a sampling of five $1 \times 1 \text{cm}^2$ solar cell devices across the diameter of the 4” wafer were tested to investigate solar cell performance and uniformity across the wafer. DJSC devices tested under one-sun AM0 conditions exhibited, on average an increase of $1.0mA/cm^2$ in $J_{sc}$ compared with the baseline device with no QDs. A reduction in $V_{oc}$ of $50mV$ was observed for the QD samples which is consistent with other reports of solar cells with the inclusion of a QD superlattice.
Fill factor was also improved by the inclusion of QDs by ~ 1%. Spectral responsivity measurements revealed an increase in sub-GaAs bandgap response indicating that collection occurred from the QD layers. A contribution of $0.02 \text{mA/cm}^2/\text{QDlayer}$ was observed for the 10x DJSC samples which was similar performance to reports in literature for a 40x QDSC which out performed a baseline GaAs cell. The improved current due to the inclusion of a QD superlattice was an important result moving toward the growth of an InGaP top junction for a TJSC device.

TJSC devices were grown similarly to the DJSC devices to determine the effect of QD inclusion to the middle cell on solar cell performance. $AM0 I-V$ results demonstrated that, while fill factor was increased by inclusion of a 10x QD superlattice, the current was not increased compared with the baseline. Furthermore, a reduction of $120 \text{mV}$ in $V_{oc}$ was observed for the TJSC device with a QD superlattice. Assuming that the DJSC structure performed similarly as both a DJSC device and as part of a TJSC device, then $70 \text{mV}$ $V_{oc}$ reduction was due to the inclusion of the InGaP top cell. This performance degradation was attributed to morphology changes due to the QD layers below the InGaP top cell and also due, possibly, to the buildup of strain from the QDs themselves. Spectral responsivity revealed sub-bandgap response from the QDs for the middle cell and integrated SR indicated an increase of $0.3 \text{mA/cm}^2$ to $J_{sc}$ for the middle junction compared with a baseline device. Integrated $J_{sc}$ for each junction indicated an increased current for the top (InGaP) and middle ((In)GaAs) cell but that the top cell was current-limiting. Thus, increase in current from the QD enhanced (In)GaAs junction was not shown in $AM0$ measurements.
5.2.2 Future Work

In order to improve the performance of DJSC and TJSC solar cell devices, an improved QD uniformity should be realized. Non-uniformity in the QD layers leads to improper strain balancing and thus degraded performance across the diameter of the solar cell. While current enhancement was observed for the 10x QD DJSC devices, a superlattice consisting of at least 40 layers was required in order to realize improved efficiency compared with a baseline device, based on integrated spectral response measurements. Thus, with adequate growth parameter adjustments such as growth temperature and alkyl flow, coupled with adequate strain balancing, a 40 layer QD DJSC device should be grown and is expected to outperform the baseline Ge/(In)GaAs device.

For triple junction solar cells, an improvement in the morphology of the InGaP top cell could improve the quality of the material and thus mitigate the $V_{oc}$ reduction experienced by the cell due to the inclusion of this top junction. Also, improved QD uniformity in the middle cell QD superlattice could help to reduce strain related defects which may have arisen due to local non-uniformities in QD density and size which affected the strain balancing condition. The growth of a well strain balanced, uniform QD superlattice containing 40 layers could possibly enhance the current enough to increase the overall device efficiency for a TJSC cell, provided that $V_{oc}$ was not significantly reduced as more QD layers were added. Improvement in the top cell material quality could also improve the current out of the device, which was a limiting factor to the performance of the TJSC devices studied.
References


