Development and Characterization of Intermediate-Band Quantum Wire Solar Cells

Colin Stuart Furrow

University of Arkansas, Fayetteville

Follow this and additional works at: http://scholarworks.uark.edu/etd

Part of the Nanoscience and Nanotechnology Commons

Recommended Citation


http://scholarworks.uark.edu/etd/1280

This Dissertation is brought to you for free and open access by ScholarWorks@UARK. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of ScholarWorks@UARK. For more information, please contact scholar@uark.edu, ccmiddle@uark.edu.
Development and Characterization of Intermediate-Band Quantum Wire Solar Cells

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Microelectronics-Photonics

by

Colin S. Furrow
The University of Southern Mississippi
Bachelor of Science in Physics, 2004
University of Arkansas
Master of Science in Microelectronics-Photonics, 2007

July 2015
University of Arkansas

This dissertation is approved for recommendation to the Graduate Council.

Dr. Gregory Salamo
Dissertation Director

Dr. Surendra Singh
Committee Member

Dr. Shui-Qing Yu
Committee Member

Dr. Morgan Ware
Committee Member

Dr. Rick Wise
Ex-Officio Member
The following signatories attest that all software used in this dissertation was legally licensed for use by Colin Furrow for research purposes and publication.

__________________________________    __________________________________
Mr. Colin Furrow, Student    Dr. Gregory Salamo, Dissertation Director

This dissertation was submitted to http://www.turnitin.com for plagiarism review by the TurnItIn company’s software. The signatories have examined the report on this dissertation that was returned by TurnItIn and attest that, in their opinion, the items highlighted by the software are incidental to common usage and are not plagiarized material.

__________________________________    __________________________________
Dr. Rick Wise, Program Director    Dr. Gregory Salamo, Dissertation Director
Abstract

The effects of a quantum wire intermediate band, grown by molecular beam epitaxy, on the optical and electrical properties of solar cells are reported. To investigate the behavior of the intermediate band, the quantum wires were remotely doped at three different doping concentrations, the number of quantum wire layers was varied from three to twenty, and the solar cell structure was optimized. For all the structures, current-voltage and external quantum efficiency measurements were performed to examine the effect of absorption and power conversion of the intermediate band solar cell (IBSC). Time-resolved photoluminescence measurements showed that δ-doping can increase the lifetime of the excited electrons in the quantum wires. The quantum efficiency measurements revealed that the quantum wires extend the absorption spectrum in the infrared and produce a photocurrent by absorption of photons with energies below the GaAs band gap energy. In addition, the quantum wire intermediate band solar cell increased the solar conversion efficiency by 13.3% over the reference cell. An increase in the quantum efficiency was observed by increasing the number of quantum wire layers in the intermediate band. Furthermore, by optimizing the solar cell structure, the quantum efficiency and solar power conversion efficiency were substantially improved. Finally, temperature dependent current-voltage measurements reveal that the quantum wire intermediate band does not degrade the temperature sensitivity of the device. This research shows the potential for a quantum wire intermediate band as a viable option for creating higher efficiency solar cell devices.
Acknowledgements

Firstly, I would like to thank God for giving his one and only Son, Jesus Christ, so that everyone who believes in Him will not perish but have eternal life and for giving me the opportunity, talent, and ability to pursue higher level education.

I would like to thank Dr. Greg Salamo for giving me the opportunity to pursue my PhD. He has always supported me and my goals, and pushed me to do my best. Dr. Salamo genuinely cares about the welfare and professional goals of his students, post-docs, and collaborators. I am eternally grateful to have him as my advisor and to have him as a friend. It has been a long, tough journey and he has been with me every step along the way.

I would like to thank Ken Vickers for accepting me into the MicroEP program, for being a great mentor, and being a great friend. We had many great conversations and he always allowed me to vent.

I would like to thank Dr. Vasyl Kunets. This research would not have been possible without his guidance, help, and mentorship. He is a great Christian, a great researcher, and a great friend. I wish him the best in his professional endeavors.

I would like to thank Dr. Russell DePriest. We had many great discussions and he is a strong Christian and I appreciate his prayers and advice.

I would like to thank all the students and post-docs who have helped me along the way, including, but not limited to: Paul, Rob, Tim, Sabina, Vitaliy, Yuriy, Mike, Thomas, Chen, Yusuke, Xian, AQ, Chris, Mourad, and Dorel.

I owe a special thanks to Renee Hearon for her concern and constant help and to me and all the other MicroEP students. She rarely gets the recognition she deserves for all the things she does to help the program and the students.
I would like to thank Dr. Rick Wise for working with me through a difficult situation and helping me to get through all the hurdles to get this dissertation completed.

I would like to thank Brother Danny Williams and the wonderful people of Sonora Baptist Church. They have always helped us, supported us, prayed for us, and treated us like family. They are some of the most thoughtful, selfless, and loving people we have been privileged to know.

Last, but not least, I would like to thank my lovely, beautiful wife, Rachel Furrow. She has been with me through the good and bad times and always supported and loved me. I love her with all my heart and always will. I could not have done this without her.

This material is based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1309989, EPSCoR Grant No. EPS1003970, and the Arkansas NASA Space Grant Consortium.
Dedication

This dissertation is dedicated to my grandparents, Evelyn and Arthur Furrow, Sr., and my parents, Linda and Arthur Furrow, Jr. You always supported me in my endeavors and believed in me.
# Table of Contents

Chapter 1: Introduction ................................................................................................................... 1
  1.1 Concept of the Intermediate Band ................................................................. 3
  1.2 Current State of the Art for Intermediate Band Solar Cells ........................ 4
  1.3 Quantum Wires .............................................................................................. 13
  1.4 GaAs (311)A Surface ..................................................................................... 15
  1.5 P-type Si-doping on GaAs (311) ................................................................. 18
  1.6 Semiconductor Solar Cells ......................................................................... 20
  1.7 Quantized Energy Levels ........................................................................... 24

Chapter 2: Molecular Beam Epitaxy ......................................................................................... 26

Chapter 3: Quantum Wire Characterization ............................................................................... 31
  3.1 Atomic Force Microscopy ........................................................................... 31
  3.2 Cross-sectional Transmission Electron Microscopy .................................. 32

Chapter 4: Results and Discussions ......................................................................................... 35
  4.1 Doping the Intermediate Band ................................................................. 38
    4.1.1 Photoluminescence .......................................................................... 39
    4.1.2 Time-Resolved Photoluminescence .................................................. 41
    4.1.3 External Quantum Efficiency .......................................................... 42
    4.1.4 Dark Current-Voltage ....................................................................... 44
    4.1.5 Illuminated I-V and Solar Conversion Efficiency ............................ 45
    4.1.6 Outcome .......................................................................................... 46
  4.2 Effect of Quantum Wire Layers on the Intermediate Band ....................... 47
    4.2.1 Photoluminescence .......................................................................... 47
    4.2.2 Transmission .................................................................................... 49
    4.2.3 External Quantum Efficiency .......................................................... 50
    4.2.4 Illuminated I-V and Solar Conversion Efficiency ............................ 51
    4.2.5 Open-Circuit Voltage and Short-Circuit Current ............................ 53
    4.2.6 Outcome .......................................................................................... 54
  4.3 Increasing Absorption in the Space-Charge Region .................................... 54
    4.3.1 Fabrication Mask Considerations ..................................................... 54
    4.3.2 Current-Voltage .............................................................................. 55
    4.3.3 Outcome .......................................................................................... 58
  4.4 Effect of Increasing the Space-Charge Field on the Intermediate Band ...... 58
    4.4.1 External Quantum Efficiency .......................................................... 58
List of Figures

Figure 1. Solar radiation spectrum.................................................................2
Figure 2. Electronic transitions involving an intermediate band.........................4
Figure 3. STM images of GaAs (311)A and lattice planes..............................16
Figure 4. P-type doping by silicon in GaAs..................................................19
Figure 5. A p–n junction in thermal equilibrium..........................................21
Figure 6. I-V curve of a diode under no illumination (black) and under illumination (red). 22
Figure 7. Top down schematic of a typical MBE growth chamber................27
Figure 8. Diagram of the RHEED diffraction from a sample..........................28
Figure 9. RHEED images of GaAs (311)A before quantum wire growth.........29
Figure 10. RHEED images of GaAs (311)A after quantum wire growth..........30
Figure 11. Island formation by strain-driven epitaxy.....................................30
Figure 12. The operating principle of Atomic Force Microscopy.....................31
Figure 13. AFM image of quantum wires....................................................32
Figure 14. Cross-sectional TEM of 10 layers of QWRs...............................33
Figure 15. Cross-sectional TEM strain profile of a quantum wire as a function of distance. 33
Figure 16. Schematic of δ-doping in the barrier layers between QWRs...........38
Figure 17. Photoluminescence of δ-doped QWR samples.............................40
Figure 18. Time-resolved PL data for the δ-doped QWR samples..................42
Figure 19. External quantum efficiency for the reference, undoped QWRs, and doped
QWRs........................................................................................................43
Figure 20. Dark I-V for samples SE159-SE165..........................................44
Figure 21. Illuminated I-V from the short-circuit current to the open-circuit voltage for SE159-SE165.

Figure 22. Photoluminescence of samples with varying layers of QWRs.

Figure 23. Transmission for GaAs (311)A substrate, reference p-i-n, and structures with 3-20 layers of QWRs.

Figure 24. External quantum efficiency for the reference p-i-n and structures with 3-20 layers of QWRs.

Figure 25. Illuminated I-V from the short-circuit current to the open-circuit voltage for the reference p-i-n and structures with 3-20 layers of QWRs.

Figure 26. Solar conversion efficiency and fill factor as a function of number of QWR layers.

Figure 27. Short-circuit current and open-circuit voltage as a function of number of QWR layers.

Figure 28. Optimized photolithography masks.

Figure 29. Dark I-V for samples SF130 and SF136.

Figure 30. Dark and illuminated I-V for samples SF130 and SF136.

Figure 31. External quantum efficiency for SF130 (Ref.) and SF136 (QWRs).

Figure 32. External quantum efficiency with applied forward bias 0-700mV for SF130 (Ref.) and SF136 (QWRs).

Figure 33. Solar conversion efficiency as a function of temperature for samples SE159-SE165.

Figure 34. Solar conversion efficiency as a function of temperature for samples SF130 (Ref.) and SF136 (QWRs).
Figure 35. Open-circuit voltage as a function of temperature for samples SE159-SE165 ..........63

Figure 36. Short-circuit current as a function of temperature for samples SE159-SE165. ..........64

Figure 37. Open-circuit voltage as a function of temperature for samples SF130 (Ref.) and
SF136 (QWRs).......................................................................................................................65

Figure 38. Short-circuit current as a function of temperature for samples SF130 (Ref.) and
SF136 (QWRs).......................................................................................................................66

Figure 39. Example of solar cell structures for δ-doped sample series. .........................68

Figure 40. Solar cell structure for varying QWR layer series.................................................69

Figure 41. Solar cell structure for enhancing the optical penetration and electric field in the
space-charge region..............................................................................................................71
Chapter 1: Introduction

The developed nations of the world all have one very important factor in common. They all depend on fossil fuels for nearly all of their energy needs. The reliance on this non-renewable energy resource manifests itself as a virtual stranglehold on society as a whole. It has an adverse global effect as a deciding factor on the alliances that are formed, the wars that are fought, the treaties that are signed, pollution, socioeconomics, and politics. The need for an economically viable, renewable form of energy grows greater each day for both developed and developing nations. Solar energy may provide one piece of the overall solution to the need for a reliable, renewable, and affordable energy mix.

Over the last decade, research in the field of solar cells has exploded. Technologies designed to increase efficiency and lower costs become more numerous and innovative each year. Current solar cell research includes a vast array of bulk and thin-film materials such as traditional Si-based photovoltaics, single-junction GaAs, triple-junction InGaP/InGaAs/Ge solar cells, cadmium-telluride, copper-indium-gallium-selenide, organic and polymer photovoltaics, conductive oxides, photochemical, and other emerging technical solutions. Solar cells using these materials all have their advantages and disadvantages, but the deciding factors for each particular application are cost and efficiency. Because of the current state of semiconductor industry, silicon based devices are the most popular due to their low-cost and adequate efficiency. However, a viable alternative to silicon based devices is emerging. Each year, more and more devices are being manufactured based on gallium-arsenide (GaAs) semiconductors. With the resulting economies of scale, costs are steadily decreasing for these GaAs based devices.
In order for solar energy to emerge from its current niche applications, it must become economically competitive with other energy sources. Today’s cheapest commercial solar cells (silicon-based) produce efficiencies of 10-20% at a cost of 13-30¢ per kilowatt-hour [1,2]. By comparison, coal and gas based power plants produce energy at a cost of 5-10¢ per KWh and nuclear energy costs are approximately 11¢ per KWh [3]. However, the energy costs from traditional power plant sources are static or increasing, while solar energy costs are decreasing. Additionally, new solar technologies are increasing solar efficiency each year. Solar energy production is increasing at an annualized rate of over 60% [1]. Many countries are investing heavily in the infrastructure for solar energy, most notably Germany.

The solar spectrum (shown in Figure 1) covers photon wavelengths from the mid-ultraviolet to the near-infrared. The arsenide-based semiconductors present a unique opportunity for implementation in solar cells because they can be alloyed with Group III metals (e.g., aluminum, gallium, and indium) and absorb light from wavelengths approximately 650 nm to 3 μm. An examination of Figure 1 indicates that solar cells made with these alloys have the potential to absorb photons from a large section of the solar spectrum.

![Solar Radiation Spectrum](image)

**Figure 1.** Solar radiation spectrum [4].
GaAs based semiconductors are well understood and have been used as photodetectors, semiconductor lasers, and other devices for years. The favorable physical properties of the GaAs in these devices can be exploited for solar cells. GaAs is a direct band gap semiconductor which allows for more efficient photon absorption in creating electron-hole pairs. In addition, the electron mobility in GaAs is up to 80 times higher than in silicon.

1.1 Concept of the Intermediate Band

For a single-junction solar cell, the theoretical efficiency limit, known as the Shockley-Quessier limit, is 40.7% [5]. The underlying reason for this limit is that only photons with energies near the band-gap energy are effectively converted. Photons with energies below the band-gap energy are physically prohibited from conversion. The concept of the intermediate band solar cell (IBSC) was proposed as a means of capturing lower energy photons of the solar spectrum, thereby enhancing the efficiency. For an intermediate-band solar cell, the theoretical efficiency limit is 63.1% [5]. This efficiency limit is similar to that of a triple-junction solar cell. An intermediate-band solar cell has an allowed electron energy band within the band gap, where the states in this band are partially occupied. As shown in Figure 2, this energy band allows for photons with energies below the band gap energy to excite electronic transitions from the valence band (VB) to the intermediate band (IB) or the intermediate band to the conduction band (CB), contributing an additional component to the overall photocurrent and conversion efficiency. In this configuration, IBSCs can produce a higher photovoltage by absorbing two sub-bandgap photons to produce an electron. A single-junction solar cell cannot supply a voltage greater than the lowest photon energy absorbed, which is the band gap energy [6].

Effectively, the presence of the IB splits the conventional semiconductor bandgap into two sub-bandgaps. This corresponds to a change in the population of carriers in the conduction,
valence, and intermediate bands. For each of these bands, they are described by different quasi-Fermi energies [7]. For IBSCs, it is very important that the quasi-Fermi energy of the intermediate band be located in the middle of the band. This ensures that, under solar spectrum illumination, there will be an equal number of available states for electrons that transition from the VB to IB as there are electrons available to transition from the IB to the CB.

![Diagram of electronic transitions involving an intermediate band.](image)

**Figure 2.** Electronic transitions involving an intermediate band.

1.2 Current State of the Art for Intermediate Band Solar Cells

The first intermediate band solar cell (IBSC) was shown in 1992. Li *et al.* showed a novel silicon solar cell that achieved a solar efficiency of 35.2% by incorporating local defect layers near the p-n junction formed by proton bombardment [8]. In 1997, Luque and Marti calculated the maximum theoretical efficiency for an IBSC as 63.1% and a tandem solar cell as 55.4% [5]. Shortly after, Marti *et al.* theoretically proposed an IBSC of quantum dots (QDs) that would produce the optimal band gaps for the IBSC of 1.24 eV from the valence band (VB) to the
intermediate band (IB) and 0.71 eV from the IB to the CB [9]. The material was composed of In$_{0.48}$Ga$_{0.52}$As QDs in Al$_{0.40}$Ga$_{0.60}$As, where the QDs had a height of 4 nm and were spaced 100 nm center-to-center. However, to achieve a condition where the IB was half-filled with electrons, the number of dopant atoms added to the QDs would be nearly two orders of magnitude higher than the number of atoms in the QD, which is impossible. Therefore, Marti et al. investigated the effect of partial filling a QD IBSC with dopants [10]. In that work, they state that quantum wells or wires cannot be used for the IB structure because they would not lead to a zero-density of states between the IB-CB and VB-IB, and that electrons would quickly thermalize between the IB and CB and would not split the quasi-Fermi levels.

As a possible alternative to QDs, Luque and Marti proposed (theoretically) the use of a metal-like intermediate band half-filled with electrons [11]. Additionally, Cuadra et al. proposed an IBSC made of type II broken band heterostructure quantum dots made of InAs and GaSb to obtain a half-filled IB [12]. This could be achieved by confining electrons and holes in different dots causing an overlap between bounded states, producing a half-filled IB and three quasi-Fermi levels.

In 2004, Luque et al. claimed that high output voltage requires the three quasi-Fermi levels [13] and is proportional to the difference between the VB and CB quasi-Fermi energy levels. Experimentally, they investigated an IBSC structure containing ten layers of InAs QDs in GaAs with a 10 nm spacer and silicon delta (δ) doping (4x10$^{10}$ cm$^{-2}$). Their QD structure showed a small increase in $J_{sc}$ of 0.2 mA/cm$^2$, with a large decrease in $V_{oc}$ of 173 mV. The quantum efficiency from the QDs sample showed a very small signal with a peak of approximately 0.05%. The purpose of their work was to present circuit representations of the equations that govern operation of the IB and verify their theoretical model. A subsequent IBSC publication by Luque et al. explored the behavior of a nonideal space-charge region with ten layers of δ-doped InAs
dots in GaAs. They showed that the reference cell had a solar power conversion efficiency of 12.1%, while the QD structure produced an efficiency of 9.3% with identical $J_{sc}$ and a large decrease in $V_{oc}$ [14]. This performance is due to an IB quasi-Fermi level that is not constant throughout the band and thus, is not half filled with electrons everywhere. They conclude that more layers of QDs and higher densities are needed. Their results point to the IB acting as a collection of non-radiative recombination centers.

Further research by Marti et al. in 2007, involving three QD IBSC structures with QD layers of 10, 20, and 50, showed that the current-voltage behavior deteriorates with more QD layers due to a degradation of $I_{sc}$ [15]. This is due to the reduction in the contribution from the p-type emitter. Their results suggest that increasing the number of layers of QDs causes an increase in strain-induced dislocations that propagate to the emitter during growth. The cross-sectional transmission electron microscopy image shows that the 10-layer structure has vertically aligned QDs and no dislocations, but the 50-layer structure shows that the growth of QDs ends after 34 layers and begins creating wetting layers and a large amount of propagating dislocations through the rest of the structure. They conclude that, in order to make practical IBSCs with larger numbers of QD layers for significant absorption of photons with energies less than the host material band gap, strain-relieving layers need to be incorporated. They further conclude that this is only feasible if InP substrates are used.

Also, in 2007 Shao and Balandin proposed a theoretical IBSC made of a three-dimensional InAs$_{0.9}$N$_{0.1}$/GaAs$_{0.98}$Sb$_{0.02}$ supracrystal with 4.5 nm tall dots spaced 2 nm apart [16]. They stated this structure creates minibands that form a quasi-IB structure with transition energies for the “VB to CB” of 1.41 eV, “VB to IB” of 0.80 eV, and “IB to CB” of 0.58 eV with a theoretical efficiency of 51.2%.
In 2008, Hubbard et al. were the first to show the effect of strain compensation on QD enhanced solar cells [17]. They produced three samples: a GaAs SC reference, an IBSC with five layers of InAs QDs with no strain compensation, and an IBSC with five layers of QDs and GaP strain compensating layers, grown by metalorganic vapour phase epitaxy (MOVPE). The QDs in these structures were 7 nm tall by 40 nm wide, with a spatial density of $5 \times 10^{10}$ cm$^{-2}$. The reference produced an efficiency of 14.7%. The uncompensated QD IBSC efficiency was 3.7% and the strain compensated QD IBSC efficiency was 10.8%. The addition of the strain compensation layers improved both $I_{sc}$ and $V_{oc}$. The uncompensated QD IBSC showed an increase in recombination in the depletion region. The diode behavior deviates from ideal due to strain-created dislocations that propagated to the emitter.

In 2009, Blokhin et al. investigated an IBSC composed of 10 layers of InGaAs QDs with no strain compensation [18]. The reference cell produced an efficiency of 23.77%, a $V_{oc}$ of 1.04 V, and a $J_{sc}$ of 27.44 mA/cm$^2$, while the QD IBSC produced an efficiency of 18.32%, a $V_{oc}$ of 0.84 V, and a $J_{sc}$ of 27.66 mA/cm$^2$. This result was the first observation of an increase in $J_{sc}$ (compared to the reference). This enhancement was due to the additional QD absorption of the infrared part of solar spectrum and effective separation of photogenerated carriers due to the formation of minibands from the array of vertically coupled QDs. The observed decrease in $V_{oc}$ and efficiency was due to recombination mechanisms (producing an ideality factor of approximately 2) and higher saturation current from the narrower band gap QDs.

In 2010, Antolin et al. attempted to mitigate strain effects in IBSCs [19]. They investigated three samples: 50 layers of InAs QDs with 83 nm spacers, 30 layers of InAs QDs with an InAlGaAs strain relief layer and 84 nm spacers, and 10 layers of InAs QDs with a 13 nm spacer. All samples were $\delta$-doped at $3-4 \times 10^{10}$ cm$^2$. The InAs/GaAs QD IBSCs showed strong carrier escape between the IB and CB. This was an indication that there was no split of the quasi-
Fermi level between the two bands. The samples with the thick spacers only exhibited thermal carrier escape from the ground state of the QDs and the sample with thin spacer showed a tunneling escape mechanism. The thermal escape from the QDs was reduced by adding a strain relief layer.

A very provocative article was published by Guimard et al. in 2010 [20]. Using metal organic chemical vapor deposition (MOCVD), they grew seven samples: a reference, three samples with 40 nm spacers (five layer of wetting layers, five layers of QDs capped to 4 nm tall, five layers of 9 nm tall QDs), and 3 samples with 11 nm spacers (five layer of wetting layers, five layers of QDs capped to 4 nm tall, five layers of 9 nm tall QDs). The reference efficiency was 13.7%. The wetting layer and capped QD samples with 40 nm spacers showed an efficiency of 13%, while the taller QD samples were 7.6%. The wetting layer and capped QD samples with 11 nm spacers showed an efficiency of 13.1%, while the taller QD samples were 9.4%. The wetting layers showed almost no enhancement to the EQE spectrum, while the capped dots extended the spectrum to 1050 nm and the uncapped dots extended to 1300 nm, with a magnitude of only 0.38% for ground state. There was almost no change in $J_{sc}$ for all samples, but the drop in $V_{oc}$ compared to the reference corresponded with the efficiency numbers and showed the trade-off between $V_{oc}$ and the extension of the absorption spectral range. The results demonstrated that these QDs did not need to meet the criteria of the IBSC model (vertical electronic coupling) to achieve high $V_{oc}$ and the QDs were vertically aligned due to strain coupling. The authors expected an enhancement of efficiency over the reference with 30 (20) layers of QDs at densities of $4 \times 10^{10}$ cm$^{-2}$ ($1 \times 10^{10}$ cm$^{-2}$).

In 2010, Jolley et al. produced ten layers of MOCVD grown In$_{0.5}$Ga$_{0.5}$As QDs producing an efficiency of 11.2%, compared to 15.3% for the reference [21]. The QDs exhibited a
reduction of the $V_{oc}$ at higher temperatures. This reduction resulted from thermal injection of carriers into the QDs, causing recombinations in depletion region.

In 2010, Zhou et al. showed an IBSC with five layers of high density InAs QDs in GaAs [22]. The QDs were 1.9 nm tall and 20 nm wide, with a spatial density of $1.1 \times 10^{11}$ cm$^{-2}$, which was the highest they achieved before cluster formation. The QD sample shows $V_{oc}$ and $I_{sc}$ degradation, but the extended absorption spectrum from the QDs produced an external quantum efficiency of 2%. The reduction in $I_{sc}$ was due to non-radiative recombination, but Zhou claimed “stacking up to a hundred layers of QDs would probably produce a prominent contribution for $J_{sc}$ enhancement, benefitting from the enhancement of the extended spectral response” [22]. Also, Zhou et al. produced another very interesting publication [23]. They used five layers of InAs QDs in GaAs to produce an IB and then investigated the presence of the IB in different parts of the structure. There were four structures: a reference, an IBSC with QDs in the intrinsic region, an IBSC with QDs in the p-doped region, an IBSC with QDs in the n-doped region, and a structure with a QD IB in all three of the regions. The best $I_{sc}$ and efficiency resulted from the structure with QDs in the intrinsic region. Surprisingly, the highest $V_{oc}$ resulted from the structure with QDs in the n-doped region. The structure with the QD IB in all three regions performed the worst. All of the QD samples showed a drop in voltage, current, and efficiency compared to the reference. The current drop from the QDs in n- and p-doped regions was due to non-radiative recombination in those regions, but the voltage was maintained.

In 2011, Bailey et al. produced InAs QD IBSCs with strain balancing layers [24]. Ten layers of InAs/GaAs QDs were incorporated into three samples: one with tall, low density dots and GaP strain balancing layers, one with small, high density dots and GaAsP strain balancing layers, and one with small, high density dots and GaP strain balancing layers. Each showed an increase in $J_{sc}$ over the reference (3.5%), but showed a small reduction in $V_{oc}$ compared to the
reference for smaller dots. Additionally, the $V_{oc}$ in all samples was very high (1.041 V for the reference and 0.994 V for the small dots) and the loss in $V_{oc}$ was attributed to an increase in dark current due to strain in the emitter. The external quantum efficiency produced by these QDs was less than 10%.

In 2011, Lu et al. investigated the temperature dependence of dark current for In$_{0.5}$Ga$_{0.5}$As/GaAs QD SCs [25]. At low temperature, the QD cell has a smaller dark current than the reference, but behaves the same as the reference over 70 K. They contend that injected carriers have a high probability to be captured by the QD potential and recombine. This process may be exacerbated when the QDs levels are unoccupied. The low ideality factor in the QDs is due to the occupation of majority carriers, leading to only one type of carrier through the depletion region causing it to act more like the quasi-neutral region. This process is highly dependent on the behavior of the QD layers at the edge of the depletion region. For low bias, the diode ideality factor was larger and dominated by recombination in space-charge region and QD layers may block lateral current flow and reduce edge recombination.

In 2011, Sablon et al. produced a study on the effect of delta-doping InAs QDs in GaAs [25, 26]. Their IBSC structures contained 20 layers of QDs where they provided a different number of electrons per dot (0, 2, 3, 6). They observed an increase in $J_{sc}$ and efficiency as the doping increases, but the $V_{oc}$ showed no trend, and the fill factor decreased. Doping the QDs decreased the spectral response of GaAs, but increased the infrared response of the dots. Additionally, the room temperature photoluminescence signal was greatly enhanced as the doping level increased. Also in 2011, Shang et al. studied the effect of the built-in electric field on QD SCs [28]. They investigated three samples: a reference, a structure with QDs in the intrinsic-region consisting of three regions of five layers of QDs, and a structure with five layers of QDs in the base (n-doped) region. The reference produced the highest efficiency (5.3%), but
the QDs in the intrinsic region produced a higher $J_{sc}$. The increase in $J_{sc}$ was due to additional electrons generated by the absorption of photons with energies below the GaAs band gap and extracted by the strong built-in electric field. However, the QD structures resulted in a lower $V_{oc}$ due to carrier trapping and recombination enhancement of the QDs. They also suggested that possible QD-induced dislocations were the cause of the reduced photovoltaic effect.

In 2012, Bailey et al. produced IBSCs composed of 10, 20, and 40 layers of InAs QDs in GaAs with GaP strain balancing layers [29]. The reference efficiency was 13.8%, and the efficiencies of the samples with 10, 20, and 40 layers were 13.4%, 12.2%, and 14.3%, respectively, and the $J_{sc}$ increased with increased QD layers. The external quantum efficiency response increased with more layers of QDs, and was much higher than previous publications, with the 40 layers of QDs showing a peak of approximately 22%. Reduced nonradiative recombination improved the $V_{oc}$, mainly from a reduction in the density of larger dots and effective strain management. Electroluminescence data indicated the primary sub-band-gap current was due to near-band-edge states (wetting layers). Also, in 2012, Shoji et al. showed the growth of 10 layers of In$_{0.4}$Ga$_{0.6}$As QDs on GaAs (311)B [30]. By investigating the effect of the spacer layer thickness, they showed that carrier lifetimes decrease as the spacer layer increases due to either size difference or electronic coupling. Furthermore, photoluminescence data showed higher energy shift in the QD peak as the spacer thickness increased.

In 2013, Linares et al. revisited the concept of creating deep-level trap states using MBE grown GaAs incorporated with titanium (Ti) to form the IB [31]. However, the decreased growth temperature required to incorporate Ti caused poor material quality from gallium vacancies and arsenic antisites. These defects caused both the IB and reference samples to show a photoresponse below the GaAs band gap and a poor EQE less than 0.1%. They also showed that the IB voltage recovered to 1.3 V under concentrated light and at low temperature. Also in 2013,
Marti et al. published an “FAQ” paper on IBSCs [32]. They claimed that it was possible to create an IBSC with deep centers (ex: Ti and Fe in GaAs) and inhibit the nonradiative recombination they produce by increasing the density. Furthermore, they claimed that the formation of a miniband has some advantages, but also reduces the effective bandgap, and is not necessary for IBSC operation. They also propose that using droplet epitaxy, as opposed to S-K growth, for QD growth may be better in reducing strain accumulation to the emitter, as well as using GaAs (311)B to achieve higher spatial densities.

Recently, Driscoll et al. [33] investigated the position and background doping effect on QD solar cells. In purely intrinsic materials, the electric field strength is uniform throughout. However, background doping shifts the electric field peak and Shockley-Read-Hall (SRH) recombination rates are altered when the peak is moved from center. They demonstrated that QDs shifted towards the emitter showed the greatest $V_{oc}$ decrease and intrinsic-region and base-shifted QDs show suppressed recombination.

In summary, some bulk materials have been shown to possess an intermediate band. However, many of these materials would not make adequate solar cells, due to a number of factors. Many of them rely on heavy ion implantation and pulsed laser annealing which leads to undesirable high defect densities. There are a couple of materials that are viable candidates as IBSCs, but recent experiments show that they exhibit efficiencies far below their potential and functional practicality.

Additionally, quantum dot intermediate band solar cells suffer from strain accumulation that can lead to the formation of defects that propagate through the intrinsic region and into the emitter, especially with more than 20 layers of QDs, and results in an increase in recombination of photo-generated carriers. Also, experiments show that photon absorption from the quantum dot states to the conduction band is weak due to the localized-to-delocalized nature [34] making
it more difficult to extract electrons from the QDs. Furthermore, high spatial densities of QDs are needed to substantially increase the photo-current. Finally, the density of states for quantum dots is a δ-function and results in a zero-dimensional density of states. Functionally, this means that the absorption spectrum of QDs is limited in spectral range.

This research proposes the use of quantum wires (QWRs), instead of quantum dots, as the material to create the intermediate band. The density of states for quantum wires leads to a much broader spectral absorption range compared to quantum dots, allowing for a larger part of the solar spectrum to be absorbed. Self-assembled quantum wires also have a higher spatial density compared to quantum dots. QWRs exist everywhere in the growth plane where the base of each wire joins the next, whereas QDs are spaced throughout the plane with spatial separations greater than several nanometers. QWRs only confine the electron wave in two directions, whereas QDs confine the electron wave in all three directions. This should allow electrons to be more easily excited from the quantum wires to the conduction band. For these reasons, quantum wires are expected to perform better than quantum dots in an intermediate band solar cell.

1.3 Quantum Wires

The implementation of nanostructures in solar cells, as hybrid energy scavengers, is drawing more attention as a means to reach higher efficiencies. Within the nanostructure class of materials, a unique importance is placed on structures that are small enough to confine the electron wave such that the energy levels are quantized. These quantum structures differ from the bulk materials because their optical and electronic properties depend more on the physical dimensions of the nanostructures than on the bulk material properties. This is due to the fact that the dimensions of these structures are on the same order as the de Broglie wavelength of the electron:
\[ \lambda_c = \frac{h}{p} \]  

(Equation 1.1)

where \( h \) is Planck’s constant, and \( p \) is the electron momentum. For example, the de Broglie wavelength of a thermal electron at 300 K is approximately 7.7 nm. The behavior and properties of these small structures are formally governed by the discipline of quantum mechanics.

In bulk semiconductors, the electron energies are a continuum of states in the valence and conduction bands with the minimum energy being that of the band gap energy. The spectrum of electron transition energy is very broad in bulk semiconductors. This can be disadvantageous in optical devices because the only way to change the absorption or emission wavelengths is to use a different material. However, through the use of quantum structures the electron energy transitions can be changed without changing materials by altering the size of the structures. This form of bandgap engineering can be accomplished by using heterostructures, such as \( \text{GaAs/In}_x\text{Ga}_{1-x}\text{As} \), to change the energy levels over several hundred meV.

Quantum structures are classified by the dimensions in which the electron is confined. Bulk materials are referred to as a 3D system, as the electron is free to move in any direction, and there are continuum energy levels. A quantum well (QW) is referred to as a 2D system, because the electron is confined in one dimension. Quantum wires (QWR) and quantum dots (QD) are considered 1D and 0D systems, respectively.

One very important property of these quantum structures is how the density of states differs from the bulk. The density of states refers to the number of states available for an electron to occupy per interval of energy. For bulk semiconductors, the density of states is continuous for all energies above the band gap. For a 2D system of quantum wells, the density of states is a step-like function and is shifted to higher photon energies (blue-shifted) because of the confinement effect. For a 0D system of quantum dots, the density of states is a delta function and
has a maximum energy shift compared to 2D and 1D systems. The density of states for a system of QWRs is delta-like with a tail at the higher energy side (low dispersion) and offers a higher density of states over a large range of energies compared to a 0D system of quantum dots. The density of states plays a critical role in the light absorption phenomena. Light absorption is a key phenomenon for solar cells, and absorption is directly related to their conversion efficiency. In this study, the QWRs are considered as a nano-medium that will play the role of the IBSC. The higher QWR density of states, compared to 0D system of quantum dots, is expected to increase the IBSC conversion efficiency.

1.4 GaAs (311)A Surface

In order to grow high-quality, low-defect, smooth, thin-film semiconductors, conventional wisdom would dictate that the crystal substrate surface be atomically flat. Typically, this is the case and great effort is made to prepare substrates to be as flat and uniform as possibly. To this point, many semiconductor devices (composed of Si, Ge, and GaAs) grown on these substrates perform very well for their intended purposes. However, in the past decade, high index surfaces have shown promise for niche applications, especially for nanostructures.

GaAs has a zinc-blend crystal structure consisting of two interpenetrating face-centered cubic lattices composed of Ga and As species. As such, the plane formed by the [100] and [010] crystalline directions is flat with a uniform distribution of either Ga and As atoms lying in the plane and is referred to as GaAs (100). This is the surface on which most device structures are grown, including many nanostructures such as QWs and QDs. However, the crystal planes that make an angle with the (100) surface have a different arrangement of atoms, such that when the bonds are broken along these angles the surfaces are no longer flat, instead, they form atomic steps.
The GaAs (311) surface, as shown in Figure 3, makes an angle of 25.2° with the GaAs (100) surface and the distribution of surface terminated atoms has changed along the [-233] direction, but not in the [01-1] direction. This anisotropy in the surface morphology was studied in detail using Scanning Tunneling Microscopy techniques and has shown that the GaAs (311)A surface possesses steps along the [01-1] direction and a terrace-like template along the [-233] under 8x1 reconstruction [35]. This surface corrugation allows for the engineering of strain and surface atom mobility to fabricate high quality one-dimensional systems.

![Figure 3](image)

Figure 3. STM images of GaAs (311)A and lattice planes. (a) STM image showing the steps along [-233] on an 8x1-reconstructed surface. (b) Atomic resolution STM image of an 8x1 reconstruction [35]. (c) Schematic cross section of the GaAs lattice viewed along [01-1] direction [36].

As previously mentioned, quantum wires confine the electron motion in two directions. This can be accomplished by either fabricating a quantum well structure into nanowires or by self-assembly. The artificial fabricating of nanowires from QWs is complicated and requires the
use of electron-beam lithography, chemical etching, and multiple growths, and greatly increases the defect and dislocation densities in these structures, not to mention a larger impact from interface states. Creating nanowires by self-assembly is more straightforward and has a lower defect density, but requires precise control of growth parameters to create the proper strain conditions.

Self-assembly of nanowires during molecular beam epitaxy (MBE) growth is based on the model of strain-driven epitaxy (Stranski-Krastanov growth). When layers of InGaAs are grown on top of GaAs, there is lateral compressive strain in the InGaAs because its lattice constant is larger than GaAs. As more monolayers of InGaAs are deposited, this lateral strain builds up until the strain is satisfied vertically by the formation of islands. For thin films grown on GaAs (100), this island formation occurs symmetrically in-plane forming pyramids, dots, etc. However, Stranski-Krastanov growth of thin films on the GaAs (311)A template surface results in strain relaxation at the condition of the enhanced atom diffusions along the preferred direction, the [-233] direction, can result in the growth of nanowires.

Such 1D nanostructures can be formed by deposition of only one strained layer. It is important to note that quantum wires can be grown on the GaAs (100) surface, but this requires complex strain engineering and growth of many layers of quantum dots at enhanced surface diffusion along the [-110] crystallographic direction to form quantum wires [37]. In addition, the QWRs grown by this method tend to be non-uniform and short in length and, obviously, contain QDs, which all may be disadvantageous. However, even for the growth of QWRs by Stranski-Krastanov growth on the template (311)A surface, improper strain engineering can lead to lattice defects. For an IBSC where QWRs will be imbedded into the GaAs reference junction, the defects can play a detrimental role and significantly degrade the IBSC conversion efficiency. In this work, detailed studies on proper strain engineering to form defect-free one-dimensional
nanostructures were performed together with identification of possible crystal defects in the IB by electrical, structural, and optical techniques.

1.5 P-type Si-doping on GaAs (311)

Typically, the p-type dopant used in GaAs and AlGaAs devices is beryllium (Be). However, Be doping does have some disadvantages. Be doping has shown high diffusion during growth and device processing causing defects and other issues [38]. This can be detrimental to the operation of devices especially under high temperature operation or if any localized high temperature regions form. During processing of the bipolar devices, rapid thermal annealing is commonly used and can cause Be atoms to diffuse through the junction interface resulting in device degradation, or even shorting the device.

As an alternative to Be doping, the idea of using all silicon doping on high-index GaAs surfaces to get p-type conductivity has been proposed. This concept has been experimentally realized in light emitting diodes on GaAs (111) [39] and InGaAs/GaAs quantum well lasers grown on GaAs (311) [40]. Kassa et al. showed that Si-doped InGaAs QW lasers grown on the GaAs (311) plane exhibited lower threshold current and higher efficiencies compared to the structures with Be as the p-type dopant [41].

Typically, during MBE growth of GaAs, the preferred growth condition is an As-rich environment, as As has a higher surface desorption rate at high growth temperatures, and the As/Ga flux ratio is above 20. Under these conditions, Si atoms will replace Ga in the lattice as the material is grown, making the material n-type. However, because of the unique bonding structure of high-index GaAs surfaces, when the As/Ga flux ratio is on the order of 8-10, dopant atoms can replace the As atoms in the lattice, making the material p-type. The range of flux ratios where this type of p-type doping occurs is small and depends very critically on growth
temperature. If the flux ratio is too low, the material will have a very high defect density. If the flux ratio is too high, the doping will be inhibited so that the resulting MBE growth results in a GaAs intrinsic material rather than a doped material. In this work, the fabrication of a p-n junction by using all silicon doping was performed. This included the growth and optimization of the GaAs n-type and GaAs p-type thick layers. The main technique for determining the material doping optimization is Hall effect measurements. The results of the Hall effect measurements for p-type Si doping in GaAs are shown in Figure 4.

![Figure 4. P-type doping by silicon in GaAs. (a) Temperature dependent mobility and (b) Temperature dependent density of holes for p-type silicon-doping in GaAs for different flux ratios.](image)

Using silicon as a p-type dopant is possible at high growth temperatures (above 600°C) with low V/III flux ratios (below 10). This method of silicon p-type doping has been shown to be successful in creating a semiconductor laser [41], but had never previously been attempted by our group or with our chamber. So, 3 samples of different V/III flux ratios (16, 7, 5) were grown to characterize the type of conductivity and mobility by temperature dependent Hall effect measurements. Each sample was fabricated into a Hall-bar structure by means of a wet chemical...
etch to define the active area and deposition of metal contacts by means of e-beam evaporating. The contacts were annealed and then measured to ensure an ohmic response. At a V/III flux ratio of 16, the Hall measurement show that both n- and p-type carriers are present. At V/III flux ratios of 7 and 5, the Hall measurement shows that the p-type carriers are dominant with effective doping levels of around 6-7 x 10^{17} cm^{-3}. At higher As flux ratios, the Si dopant atoms produce both n- and p-type carriers.

1.6 Semiconductor Solar Cells

A solar cell is simply a photovoltaic material that uses photons supplied by the sun to excite free electrons into the conduction band (or holes to the valence band), thus creating an electrical current. To direct and control this electrical current, a p-n junction (or diode) is used. This p-n junction is the result of the joining of a semiconductor with excess holes (p-type) and a semiconductor with excess electrons (n-type). The theory of semiconductor and diode physics is very deep and extensive, so an overview of the key components needed to understand and characterize the behavior are presented as follows.

When two doped semiconductors are joined together, there is an abrupt change in doping at the interface. As such, majority carrier electrons from the n-type region will diffuse to the p-type region and, conversely, majority carrier holes from the p-type region will diffuse to the n-type region. This process leaves behind positively charged donor atoms in the n-type region and negatively charged acceptor atoms in the p-type region. This results in a space-charge region (also known as the depletion region) and an electric field that pushes electrons and holes from this region. At thermal equilibrium, this space-charge electric field is balanced by the majority carrier density gradient. This situation is shown in Figure 5.

In an ideal diode, the total current in response to an externally applied voltage is:
\[
I = A \left[ \frac{q D_p p_{n0}}{L_p} + \frac{q D_n n_{p0}}{L_n} \right] \exp \left( \frac{q V_a}{n k T} \right) - 1
\]  
(Equation 1.2)

where \( A \) is the area of the device, \( q \) is the electron charge, \( D_p \) and \( D_n \) are the hole and electron diffusion coefficients, \( p_{n0} \) and \( n_{p0} \) are the thermal equilibrium minority carrier concentrations in the n and p regions, \( L_p \) and \( L_n \) are the minority diffusion lengths in the n and p regions, \( V_a \) is the externally applied voltage, \( n \) is the diode ideality factor, \( k \) is Boltzmann’s constant, and \( T \) is the temperature.

\[ \begin{align*}
\text{neutral region} & \quad \text{space charge region} & \quad \text{neutral region} \\
\text{holes} & \quad \text{electrons} & \\
\text{carri er concentration [log scale]} & \\
\text{E-field} & \quad \text{E-field force on holes} & \quad \text{E-field force on electrons} \\
\text{"Diffusion force" on holes} & \quad \text{"Diffusion force" on electrons} \\
\end{align*} \]

**Figure 5.** A p–n junction in thermal equilibrium.

The total current density is controlled by the drift currents of minority carriers in the depletion region. So when the applied voltage is zero, no current flows through the diode. The expression in Equation 1.2 shows the behavior of the current as function of the applied voltage, providing the current-voltage (I-V) characteristics that can be directly measured.
When the diode is under constant illumination, the steady-state current density across the device is:

\[ I_L = qAG(W + L_n + L_p) \]  
(Equation 1.3)

where \( G \) is the generation rate and \( W \) is the width of the device. Therefore, the total current for the diode is:

\[
I = I_0 \left[ \exp\left( \frac{qV_a}{nkT} \right) - 1 \right] + qAG(W + L_n + L_p) = I_0 \left[ \exp\left( \frac{qV_a}{nkT} \right) - 1 \right] + I_L \]  
(Equation 1.4)

The effect of illumination on the diode causes the device to operate in reverse bias and results in the current being displaced by \( I_L \), as shown in Figure 6.

![Figure 6. I-V curve of a diode under no illumination (black) and under illumination (red).](image)

To characterize the effect that light has on the device current, an examination of the I-V curve under illumination is required. The point of interest on the curve is when the power produced is at a maximum, where \( V = V_{MP} \) and \( I = I_{MP} \). This point defines a rectangle whose area
is given by $P_{MP} = V_{MP}I_{MP}$, and is largest rectangle at any point on the I-V curve [42]. The rectangle formed by the open-circuit voltage ($V_{oc}$) and the short-circuit current ($I_{sc}$) provides a measure of the ideality of the diode. The fill factor (FF) is a ratio of these two rectangles and provides a measure of the squareness of the I-V curve. The fill factor is defined as:

$$FF = \frac{P_{MP}}{V_{oc}I_{sc}} = \frac{V_{MP}I_{MP}}{V_{oc}I_{sc}}$$  \hspace{1cm} (Equation 1.5)

By definition, the fill factor will always be less than 1. Possibly the most important figure of merit for a solar cell is the power conversion efficiency ($\eta$). This efficiency is defined as:

$$\eta = \frac{P_{MP}}{P_{in}} = \frac{FFV_{oc}I_{sc}}{P_{in}} = \frac{V_{M}I_{M}}{P_{in}}$$  \hspace{1cm} (Equation 1.6)

In a perfect diode, the displacement of $I_L$ would directly correspond to how efficiently light is converted into electrical current. However, in reality there are mechanisms within these materials that can affect the device current by altering the recombination rates of the excess carriers. Defects in the semiconductor material can provide trap states in the band gap and act as recombination centers. According to the Shockley-Read-Hall (SRH) theory, the excess minority carrier lifetime is inversely proportional to the density of trap states.

Another source of unwanted recombination centers are surface states. In real applications, the crystal structure of the material is not infinite, and the abrupt ending of the crystalline lattice results in a distribution of energy states in the band gap. The density of states at the surface is larger than in the bulk, and this larger density of states results in a shorter lifetime for the excess minority carriers at the surface. These effects can be seen in both dark and illuminated I-V curves, in both forward and reverse bias. One of the primary sources of loss during illumination of a solar cell is leakage current. Leakage current mainly occurs in reverse operation and can be due to many factors, such as doping profile, dopant concentrations, defects, junction parameters,
and device processing of metal contacts. This leakage current affects the generation and recombination rates and the lifetime of the minority carriers.

1.7 Quantized Energy Levels

In bulk semiconductors, the band gap of the band material depends on the material properties. Therefore, electronic transition energies are a continuum above the band gap energy and conduction of electrons occurs at the lowest unfilled state in the conduction band. The electronic wave functions in these bulk semiconductor crystals are Bloch waves dependent on the crystalline lattice and atomic species composing the crystal. However, as previously mentioned, when the dimensions of these materials are reduced down towards the same order of magnitude as the electron de Broglie wavelength, the electronic wave function can be confined. This confinement causes the electronic wave functions and associated energy levels to depend on the size of the material. As a result, the electronic energy levels separate from a continuum to quantized (or discrete) energy levels.

The energy levels of the quantum wires in this research can be approximated by the “Particle in a Finite-Walled Box” situation. Similar to the solutions of the more commonly known “Particle in a Box” problem (with an infinite barrier), the solutions for the wave functions are sine and cosine functions inside of the potential well. However, the wave functions of the “particle in a box” do not extend into the barrier. With a finite barrier, the wave function has an exponentially decaying tail that extends into the barrier some small distance. This means that the there is a non-zero probability for the particle to be found in the potential barrier. This is what allows for the lateral coupling of quantized states. If two finite-walled boxes are in close proximity, such that the exponentially decaying tails overlap, the wave functions and energy levels become coupled. By repeating this situation with many finite-walled boxes, the system no
longer behaves like individual “boxes”, but rather as one coupled system where the energy levels and wave functions extend across the entire system. This scenario is what allows for the creation of an intermediate energy band below the band gap of the barrier material.
Chapter 2: Molecular Beam Epitaxy

Molecular Beam Epitaxy (MBE) is an epitaxial method of replicating crystalline materials in an ultra-high vacuum chamber. In this replication, or growth, of these crystalline materials, atomic or molecular beams are directed towards a heated substrate. These atoms or molecules impinge on the surface, where they can diffuse along the surface, react with vacancies in the lattice, and incorporate into the crystal matrix. The mean free path of impurities in the MBE chamber is longer than the distance from the source materials to the substrate under ultra-high vacuum conditions. The semiconductor materials used for this research were grown using a Riber [43] 32P solid source MBE Chamber located in the Nano building at the University of Arkansas.

This particular MBE chamber consisted of a spherical stainless steel main housing with the following main components: cryoshrouds, effusion cells and shutters, RHEED gun and phosphor screen, BandiT system, ion gauge, mass spectrometer, wafer substrate holder and manipulator, and an ion pump. A diagram of this system is shown in Figure 7. Liquid nitrogen flowed through the cryoshrouds to cool down the inner walls of the chamber to 77 K so that unwanted materials in the chamber would stick to the walls. The effusion cells contained crucibles filled with the source materials of the crystalline materials and dopant materials, usually in the pure metallic form (Al, Ga, Si, etc.). The temperature of the crucibles was controlled and regulated by a power supply and thermocouple. Mechanical shutters at the opening port of the effusion cells were used to control the on/off function of the molecular beams produced by the effusion cells.

The KSA BandiT system “is a non-contact, non-invasive, real-time, absolute wafer and film temperature monitor used during thin-film deposition” [44]. The BandiT system provided
accurate and repeatable temperature information from the infrared blackbody emission of the GaAs band edge, that was correlated with the thermocouple reading and oxide desorption information.

**Figure 7.** Top down schematic of a typical MBE growth chamber [45].

The chamber pressure was monitored by an ion gauge, which also gave the partial pressure of atoms/molecules for flux measurements. The wafer substrate holder and manipulator allowed for loading/unloading of the sample (on molybdenum blocks) and was rotated during growth to improve spatial uniformity. The chamber was pumped down to ultrahigh vacuum by an ion pump. The ion pump trapped particles by using an electronic discharge to ionize atoms and molecules in the chamber. These ionized atoms were accelerated by an electric field and became imbedded into the walls of the pump or collected by a chemically active cathode.

Reflection high-energy electron diffraction (RHEED) is a technique which gives information about the surface structure of the crystal. High-energy electrons are generated and
accelerated by the electron gun. These electrons are directed towards the sample at a glancing angle and diffract off of the surface. The scattered electrons constructively interfere and impinge on a phosphor screen opposite the electron gun as shown in Figure 8.

![Diagram of the RHEED diffraction from a sample](image)

**Figure 8.** Diagram of the RHEED diffraction from a sample [46].

Once the substrate was transferred to the MBE, the substrate was slowly heated to observe the oxide layer on the surface desorb. This was done by monitoring the RHEED pattern on the [-110] crystal direction. As the temperature increased above 480 °C, the intensity of the interference fringes slowly increased as the rough oxide layer desorbed until the desorption temperature was reached, at which point there was a sharp transition and the intensity increased exponentially. For GaAs, the oxide desorption temperature is well known (582±1 °C) and represents the “true” substrate temperature. The oxide desorption temperature was correlated to the BandiT and thermocouple reading to find the approximate temperature offset for the growth temperature ranges. Typically, bulk GaAs grows well at the desorption temperature. After observing the oxide desorption, the temperature was increased by 30 °C for 10 minutes to ensure that the entire oxide layer was fully removed.
After this process was complete, a 500 µm buffer layer of GaAs was grown at the desorption temperature (~580-585 °C) to ensure a smooth, high-quality surface. At this temperature, the GaAs (311)A surface had a 4x1 lattice phase (Figure 9a and 9b). Then the temperature was decreased to 540 °C, undergoing a phase transition to 8x1 lattice reconstruction (Figure 9c). This was the preferable lattice reconstruction and growth temperature range (~520-540 °C) for the formation of self-assembled quantum wires.

Figure 9. RHEED images of GaAs (311)A before quantum wire growth. (a) GaAs (311)A surface along [-233] at 585 °C. (b) GaAs (311)A surface along [-110] at 585 °C. (c) GaAs (311)A surface along [-110] at 540 °C.

As the InGaAs was deposited on the surface, the RHEED pattern intensity decreased as the adatoms impinged on the surface. The in-plane lattice constant of InGaAs was larger than the host GaAs matrix, causing compressive strain on the surface. As more InGaAs material was deposited, the compressive strain reached a point where the energy was too large to continue replicating the lattice. As more InGaAs material was deposited, the compressive strain reached a point where the energy was too large to continue replicating the lattice. This energy was relieved through the formation of islands, where the surface energy of the islands matched the compressive strain in the lattice. This process is shown in Figure 10. For an isotropic surface, this process would form quantum dots.

However, the GaAs (311)A surface with an 8x1 lattice phase is highly anisotropic. The mobility of the surface atoms was enhanced along the [-233] direction and suppressed along the
[-110] elongating the islands. With enough material deposited, at the appropriate conditions, this elongation can stretch over several microns, forming nanowires. For the InGaAs QWRs, the RHEED pattern in Figure 11 shows the faceting along the [-110] direction. For the Atomic Force Microscopy characterization samples, 11 monolayers of In$_{40}$Ga$_{60}$As material were deposited to form the self-assembled quantum wires.

![Diagram](image)

**Figure 10.** Island formation by strain-driven epitaxy.

![Images](image)

**Figure 11.** RHEED images of GaAs (311)A after quantum wire growth. (a) GaAs (311)A surface along [-110] at 540 °C after QWR deposition. (b) GaAs (311)A surface along [-233] at 540 °C after QWR deposition.
Chapter 3: Quantum Wire Characterization

3.1 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a type of Scanning Probe Microscopy that can measure local surface properties as it raster-scans a two-dimensional area. The Bruker [47] Nanoscope V has the capability to scan and simultaneously collect information about surface height, phase, magnetism, etc. For the purpose of characterizing nanostructures, the AFM is capable of producing high-resolution topographical images with sub-Angstrom resolution. The operating principle behind the AFM is shown in Figure 12.

![Figure 12. The operating principle of Atomic Force Microscopy [48].](image)

The AFM probe is a cantilever with an atomically sharp tip on the bottom of the free end. A laser is aimed on the back of the tip near the end of the cantilever and the reflection impinges on a two-dimension detector. As the tip moves across the surface, the deflection of the cantilever is measured on the detector.
The “tapping mode” is the AFM scanning mode that was used in this research. In this mode, the cantilever is driven to oscillate slightly below the resonance frequency. The probe lightly taps the surface of the sample during measurements, and the amplitude of the oscillation is measured from the interaction. The tapping mode has high lateral resolution and causes less damage to the samples, although the scan speed is slightly slower than the contact mode. After deposition of 11 monolayers of In$_{40}$Ga$_{60}$As, the AFM scan (Figure 13) showed that the quantum wires had a height of ~3-4 nm and a base of ~50 nm.

Figure 13. AFM image of quantum wires. (a) AFM scan image of QWRs. (b) Height profile of QWRs across the AFM scan.

3.2 Cross-sectional Transmission Electron Microscopy

After growth of the IBSCs, the method of Cross-sectional Transmission Electron Microscope (X-TEM) was used to verify the quality of the material and the dimensions of the imbedded quantum wires. The QWRs imbedded in the device maintained the same dimensions as the QWRs grown for surface topographical characterization, as shown in Figure 14. In the X-TEM images, there were no visible structural defects. X-TEM also allowed for nanoscale stain
mapping, as shown in Figure 15. Even though the QWRs were only approximately 3-5 nm tall, the strain profile existed over 16-17 nm.

![Figure 14. Cross-sectional TEM of 10 layers of QWRs.](image)

![Figure 15. Cross-sectional TEM strain profile of a quantum wire as a function of distance. The inset shows the indium composition (red).](image)
During growth, as the lattice mismatched InGaAs material was deposited on a GaAs matrix, the surface InGaAs lattice was compressively strained. When that compressive strain was relieved by the formation of QWRs, the lattice in the InGaAs was relaxed at the surface. As a consequence, the InGaAs strained the host GaAs lattice on which it was formed, leading to tensile strain in the GaAs. Furthermore, once the InGaAs QWRs were formed, more GaAs material was deposited on top of the wires. This GaAs was also strained (tensile) to the InGaAs QWR lattice for several nanometers until the lattice could relax to its natural lattice constant. When growing several layers of InGaAs QWRs, separated by a GaAs spacer, each layer of QWRs needed to be well outside of this strain field. If the QWR layers were too close to this strain field, strain-related defects could appear and/or quantum dots could be formed instead of quantum wires. Therefore, the GaAs spacer layer between QWR layers should be at least 20 nm based on the strain profile.
Chapter 4: Results and Discussions

The focus and goal of this research was to develop and demonstrate: (1) the first quantum wire intermediate band solar cell and (2) demonstrate that the solar efficiency of the cell is higher than the exact same cell (reference cell) without the intermediate band. These goals were accomplished by growth of the cell structure via molecular beam epitaxy, morphological characterization, and optical and electrical measurements.

In addition, after demonstrating the two major goals of the research and the corresponding performance of the quantum wire intermediate band solar cell, improving the performance by changing and varying several parameters of the cell was also investigated. Those changes led to uncovering some of the underlying physics of the intermediate band concept. In particular, to improve on the dissertation and on the first quantum wire intermediate band solar cell performance, the role of some of the most important parameters were investigated. Those include:

1. **Doping the intermediate band.** Increasing the electron concentration in the intermediate level is an obvious way to enhance the IB-to-CB electronic transition. Of course there is some balance between the VB-to-IB and IB-to-CB that must be found. It is also true that doping introduces defects and scattering sites which reduces the number of carriers or current collected for a given solar flux. For this reason, a range of different doping levels were explored.

2. **Varying the number of QWR layers comprising the intermediate band.** Increasing the number of QWR layers would of course increase the overall absorption at photon energies below the GaAs band gap energy and increase the solar efficiency proportionally.
3. *Fine tuning the device structure.* Adjusting the thickness of the material preceding the space charge region can be used to increase the solar flux penetration and photon absorption into the space-charge region. More solar light in the space charge region will increase the solar cell current.

4. *Increase the electric field in the space charge region.* Increasing the electric field means that the carrier velocity can increase resulting in an increase in the extraction of photo-generated carriers from the depletion region.

5. *Control of the effect of temperature changes on the sensitivity of the solar cell.*

Semiconductor performance, and therefore solar cells based on semiconductors, is sensitive to temperature changes. For example, increases in temperature reduce the band gap and therefore open circuit voltage, while increased phonon scattering decreases the short circuit current. Since climate temperature variations are expected and even controlled for solar farms, it is important to limit the temperature sensitivity of the intermediate band solar cell. Although in this work the sensitivity could not be controlled, in all cases it was at least no worse than the reference cell.

To explore these five features several different measurement probes were used, including: (a) photoluminescence; (b) time-resolved photoluminescence; (c) absorption and transmission; (d) open-circuit voltage and short-circuit current; (e) current-voltage curves; (f) external quantum efficiency; (g) solar conversion efficiency; (h) dark current; and (i) the nature of the fabrication mask. While each of these probing tools are valuable, a different selection from this list was used for each the demonstration of the quantum wire intermediate band solar cell and for the five steps taken to improve on the performance.

The research here was explored using several probes on three different sets of samples which had a specifically designed structure that provided a standard reference sample for
comparison. The sets were created to study (1) delta doping; (2) multilayered quantum wires; and (3) control of absorption and space charge field.

The investigation on the quantum wire intermediate band solar cell and the five steps taken to improve its performance using several specific probes on three sets of samples is described in detail below. This is followed by a full description for each set of samples.

The first quantum wire intermediate band solar cell demonstrated a higher solar efficiency than the exact same cell (reference cell) without the intermediate band. This was accomplished based on fabrication of a GaAs p-i-n solar cell with an intermediate band in the junction device.

The intermediate band, comprised of QWRs, resulted in devices demonstrating nontrivial enhancements in solar cell conversion efficiency over the reference cell. In particular, the insertion of quantum wires into a p-i-n junction resulted in an increase of the solar cell efficiency up to 5.1% compared to 4.5% for the reference p-i-n GaAs solar cell. The presence of the quantum wire intermediate band resulted in an increase of the short circuit current with almost no degradation of open circuit voltage. In fact, this enhancement was the result of an increase in short circuit current due to the presence of the intermediate band with a comparatively small reduction, 20–50 mV, in the open circuit voltage. This was an order of magnitude less than the reduction in $V_{oc}$ in comparable QD devices, which normally show a loss of efficiency. The determining difference between QD and QWR based intermediate band devices is believed to be the significantly larger density of states of the QWRs resulting in an increase in the external quantum efficiency and, thus, the effective illumination intensity of the device. This intermediate band is preferred for absorption of normal incident light and allows the lateral transport for photo-generated carriers. Those preliminary results suggested that the doping of the intermediate
band in this system should play a crucial role in solar cell performance and should be studied next.

4.1 Doping the Intermediate Band

The operation of the intermediate band requires a two-step electronic excitation process from the valence band to the intermediate band and from the intermediate band to the conduction band. Ideally, these two processes should happen independently. This requires that the intermediate band be half-filled with electrons. Bulk MBE-grown GaAs has an unintentional p-type background doping level of $\sim 10^{14}$-$10^{16}$ cm$^{-3}$, mainly due to carbon acceptor impurities. This results in holes occupying the quantized states in the valence band of the InGaAs quantum wires.

Therefore, electrons must be provided to the intermediate band to enhance the absorption processes. In this research, this was accomplished by the use of remotely $\delta$-doping the IB. The technique of remote $\delta$-doping involves placing a two-dimensional “sheet” of electrons in close proximity to the QWRs, in the barrier layer separating the QWR layers, as shown in Figure 16.

![Figure 16. Schematic of $\delta$-doping in the barrier layers between QWRs.](image)
By δ-doping in the barriers surrounding the quantum wires, electrons are provided to the quantum wire states (through diffusion) without introducing doping-related defects into the quantum wires themselves. It was expected that the addition of electrons to the IB would enhance the absorption process of the IB.

4.1.1 Photoluminescence

The quantum wire intermediate band should produce energy levels below the GaAs band gap energy. To investigate the presence of these intermediate energy levels, photoluminescence spectroscopy measurements were performed. Photoluminescence (PL) spectroscopy is a nondestructive method of probing the optically active electronic transitions of a material. Typically, for semiconductors, high energy laser light is incident on the sample and is absorbed. The absorption of the photon energy excites electrons high in the conduction band. The energetic electrons can travel through the material, dissipating excess energy through radiative and non-radiative relaxation processes. For radiative relaxations, the electrons transition from an excited state to the equilibrium state by emitting photons with energies that relate to the difference in energy levels of the electronic states. By detecting the spectra of the emitted photons, information about the energy levels of the bulk and nanostructure material systems can be deduced.

To measure the PL spectra, the samples were mounted in a closed-cycle helium cryostat, allowing for measurements at 10 K. For excitation above the GaAs band gap, a 532 nm continuous wave Nd:YAG laser was used. The PL emission signal was dispersed by a triple grating monochromator and detected by a liquid nitrogen cooled InGaAs linear photodiode array. The results are shown in Figure 17.
The quantum wires produced optical active energy bands that existed at energies below the GaAs bandgap. The lowest energy peak for the undoped quantum wires occurred at 1.34 eV with a second peak at 1.41 eV. The lowest and middle δ-doped QWRs also had a low energy peak at 1.34 eV and a second peak at 1.41 eV. The highest δ-doped QWRs had a low energy peak at 1.36 eV and a second peak at 1.4 eV. Those results agreed with previously published QWR results of the same composition [47–50] and confirmed the existence of the QWR intermediate band.

**Figure 17.** Photoluminescence of δ-doped QWR samples. (a) PL of the undoped QWRs. (b) PL of the δ-doped QWRs for \( N_D = 6.7 \times 10^{10} \text{ cm}^{-2} \). (c) PL of the δ-doped QWRs for \( N_D = 1.0 \times 10^{11} \text{ cm}^{-2} \). (d) PL of the δ-doped QWRs for \( N_D = 5.0 \times 10^{11} \text{ cm}^{-2} \).
4.1.2 Time-Resolved Photoluminescence

With the existence of the QWRs confirmed, the lifetime of the electrons excited to these energy levels had to be measured. In the operation of the solar cell, the optically excited electrons in the conduction band had to have a long enough lifetime to be able to traverse the depletion region and contribute to the current extracted from the device. The method for measuring these lifetimes was by time-resolved PL measurements. The experimental setup for time-resolved PL was similar to the PL setup previously described. However, the excitation wavelength was changed to 850 nm (1.45 eV), which is below the GaAs band gap energy, so that only electronic transitions in the intermediate band were excited. The bandwidth of the detector was reduced to only measure the emission signal from the lowest energy level in the QWRs, and the signal intensity was measured as a function of time for different excitation intensities. The results are shown in Figure 18.

The slope of the signal decay yields the lifetime. The undoped wires had an average ground state lifetime of 670 ps. The lowest δ-doped QWRs enhanced the lifetime to 764 ps. The middle δ-doped QWRs had a lifetime of 491 ps. The highest δ-doped QWRs had a lifetime of 296 ps. The diffusion length of the electrons is given by the following expression:

\[ L_n = \sqrt{D_n \cdot \tau_n} \]  

(Equation 4.1)

where \( \tau_n \) is the lifetime of the excited electrons and the electron diffusion coefficient, \( D_n = 200 \) cm²/s. The diffusion length for the undoped QWRs was 3.7 µm. The diffusion lengths for the low, mid, and high level δ-doped QWRs were 3.9, 3.1, and 2.4 µm, respectively. All of these diffusion lengths were longer than the width of the depletion region by a factor of 5 or greater.
Figure 18. Time-resolved PL data for the δ-doped QWR samples. (a) Time-resolved PL of the undoped QWRs. (b) Time-resolved PL of the δ-doped QWRs for $N_D = 6.7 \times 10^{10}$ cm$^{-2}$. (c) Time-resolved PL of the δ-doped QWRs for $N_D = 1.0 \times 10^{11}$ cm$^{-2}$. (d) Time-resolved PL of the δ-doped QWRs for $N_D = 5.0 \times 10^{11}$ cm$^{-2}$.

4.1.3 External Quantum Efficiency

To investigate the efficiency of extracting electrons from the device, the external quantum efficiency was measured. Quantum efficiency (QE) is basically the percentage of photons that produce charge carriers in the device. QE is measured by scanning over a large spectral range to characterize the device efficiency at each photon energy/wavelength. The external quantum efficiency (EQE) is the percentage of charge carriers generated to the number of photons (of a given energy) incident on the device. Measuring the EQE of the IB structures provides details about the VB→IB, IB→CB, and VB→CB transitions, as well as any transitions
involving defect states. EQE measurements were performed using a PV Measurements, Inc. [53] QEX10 system. The samples were measured at room temperature, with an excitation wavelength from 300 nm to 1100 nm in 5 nm increments, at zero externally applied bias. The results of EQE measurements are show in Figure 19. The undoped QWRs had a peak EQE of 11.3%. The low, mid, and high level δ-doped QWRs had peak EQE of 9.9%, 10.3%, and 7.5%, respectively, at a wavelength of 905-910 nm.

**Figure 19.** External quantum efficiency for the reference, undoped QWRs, and doped QWRs.

The effect of δ-doping the QWRs was a reduction of the efficiency of extracting electrons from the quantum wire states. The EQE of the bulk GaAs was reduced by the presence of the undoped QWRs. This indicates that the QWRs act like traps for electrons in the conduction band produced by the valence band to conduction band excitation in the GaAs. In the δ-doped QWR samples, the reduction of the GaAs EQE signal was reduced due to partial filling of the QWR states by electrons, causing the carrier capture to be less efficient [54].
4.1.4 Dark Current-Voltage

The current response to an applied external electric field gives information about the transport mechanisms. In diodes, current in the space-charge region is controlled by generation-recombination of minority carriers and is the dominant current mechanism at low forward-bias voltage. At higher voltages, the current is dominated by the behavior of majority carriers in the quasi-neutral regions. To investigate and characterize ideality of the diode behavior, dark current-voltage (I-V) measurements were performed. The current-voltage (I-V) data was obtained by using computer controlled Keithley [55] voltage source and current source measure unit. Results of the I-V data for the samples are presented in Figure 20.

Figure 20. Dark I-V for samples SE159-SE165.
The diode ideality factor, $n$, is given by the following equation:

$$n(V) = \frac{d(V/V_t)}{d(\ln(I))}$$  \hspace{1cm} (Equation 4.2)

where the thermal voltage is given by, $V_t = q/k_B T = 26$ mV, at 300K. There are three distinct regions of interest which show different phenomena contributing to the device current. From $0 < V < 0.2$, all samples showed the current generation due to band-to-band electron generation-recombination events in the space-charge region. From $0.2 < V < 0.6$, the two references and the undoped quantum wires exhibited similar current behavior of different magnitudes. However, the doped quantum wires showed a much different current behavior with an $n < 2.5$. Typically, this is an indication of strong SRH recombination and Auger recombination events. For $V > 0.6$, the current was limited by the series resistance of the diode and circuit. The reference p-n diode had a diode ideality factor of $n = 2.4$ below 0.62 V. The reference p-i-n diode exhibited a similar behavior with $n = 2.3$ at a bias voltage in the range of $0.22 < V < 0.62$. This was due to recombination in the bulk GaAs.

4.1.5 Illuminated I-V and Solar Conversion Efficiency

To obtain the effect of these diode structures under solar illumination, the I-V behavior was investigated, using the Keithley system previously described. For simulating the solar spectrum, a lamp producing the air mass 1.5 (AM1.5) spectrum was used at a calibrated intensity of 100 mW/cm$^2$ (1 sun). These I-V measurements were performed at room temperature and are shown in Figure 21.

The I-V of all the samples under illumination show normal solar cell behavior. The standard p-n junction had the lowest efficiency of 2.6%. The standard p-i-n reference had a
higher $V_{oc}$ and $I_{sc}$, resulting in an efficiency of 4.5%. The undoped QWRs exhibited a higher $I_{sc}$, with only a 20 mV drop in $V_{oc}$, resulting in an efficiency of 5.1%. The mid-level $\delta$-doped QWRs showed a slight drop in $I_{sc}$ versus the undoped wires and a $V_{oc}$ drop of 50 mV resulting in an efficiency of 5.0%. The low and high $\delta$-doped QWRs exhibited efficiencies of 3.7% and 3.5%, respectively. All of the QWR samples showed an increase in $I_{sc}$. This is due to electronic transitions for photons below the GaAs band gap energy created by the quantum wire intermediate band.

**Figure 21.** Illuminated I-V from the $I_{sc}$ to the $V_{oc}$ for SE159-SE165.

4.1.6 Outcome

The results demonstrated in this section identify the energy levels of the quantum wires
that lie in the band gap of GaAs. The lifetime of electrons excited to the quantum wire states are shown, along with the dependence of lifetime as a function of δ-doping. From these lifetimes, the diffusion lengths were calculated and shown. Based on these values, the QWRs could be highly δ-doped before the diffusion length was equal to the length of the space-charge region. This is important because doping of the intermediate band is theoretically necessary to achieve the optimal intermediate band performance. The presence of the quantum wires improved the solar cell efficiency while δ-doping decreased the role of the quantum wires as traps. While the quantum wires broadened the absorption spectrum, the external quantum efficiency of the quantum wires due to δ-doping did not increase as expected.

4.2 Effect of Quantum Wire Layers on the Intermediate Band

Another method to increase the absorption of the intermediate band is to change the number quantum wire layers. It was expected that by increasing the number of QWR layers, that the absorption would increase proportionally. To investigate this effect, the number of quantum wire layers was varied from 3 to 20.

4.2.1 Photoluminescence

As previously described, the PL experiments were performed at 10 K to observe the energy level structure of the intermediate band. The results are shown in Figure 22. For the samples with 3, 5, 10, 15, 20 layers of QWRs, the lowest peak existed at 1.35, 1.30, 1.31, 1.29, and 1.31 eV, respectively, as well as a second peak at 1.38, 1.38, 1.35, 1.38, and 1.35 eV, respectively.
Figure 22. Photoluminescence of samples with varying layers of QWRs. (a) PL of the reference p-i-n. (b) PL of the p-i-n with 3 layers of QWRs. (c) PL of the p-i-n with 5 layers of QWRs. (d) PL of the p-i-n with 10 layers of QWRs. (e) PL of the p-i-n with 15 layers of QWRs. (f) PL of the p-i-n with 20 layers of QWRs.
4.2.2 Transmission

To complement the PL data, optical transmission experiments were performed to show the absorption behavior as a function of the number of QWR layers. These results are shown in Figure 23. The transmission spectrum was reduced below the GaAs band gap due to the QWRs. At 910 nm, where there was a strong response from the QWRs, the p-i-n had a transmission of 45.6%, 10 layers of QWRs had a transmission of 42.8%, and 20 layers of QWRs had a transmission of 39.2%. The QWRs showed absorption of light with a lower energy than the GaAs band gap energy. Compared to the GaAs p-i-n, the addition of 10 QWR layers and 20 QWR layers lowered the transmission by 2.8% and 6.4%, respectively.

**Figure 23.** Transmission for GaAs (311)A substrate, reference p-i-n, and structures with 3-20 layers of QWRs.
4.2.3 External Quantum Efficiency

As previously described, EQE measurements were performed using a PV Measurements, Inc. QEX10 system. The samples were measured at room temperature, with an excitation wavelength from 300 nm to 1100 nm in 5 nm increments, at zero externally applied bias. The results of EQE from the samples are shown in Figure 24.

![External Quantum Efficiency](image_url)

**Figure 24.** External quantum efficiency for the reference p-i-n and structures with 3-20 layers of QWRs.

The reference sample (with no QWRs) showed the highest EQE response above the GaAs band-gap energy at ~38%. All of the QWR samples showed an EQE response at energies
below the GaAs bandgap energy and showed multiple sub-band transitions of QWR states. There was a very clear trend that with an increasing number of QWR layers, the EQE increased. At energies below the GaAs band gap, the structures with 3, 5, 10, 15, and 20 layers of QWRs produced a peak EQE of 3.3, 5.6, 8.2, 14.8, and 18.8%, respectively, which was nearly linearly proportional.

In all of the QWR samples, there was a degradation of the bulk GaAs EQE signal of ~1-2%. This suggested that the presence of the QWRs caused recombination sites at excitation energies above the GaAs band gap. This could have been due to the presence of strain-related defects in the GaAs layers in the depletion region or due to the energy levels in the QWRs. As previously stated, there was a strong indication of recombination processes due to the QWRs.

4.2.4 Illuminated I-V and Solar Conversion Efficiency

For simulating the solar spectrum, the illuminated I-V measurement procedure previously described was used. Figure 25 shows the forward-bias I-V results for these samples, under illumination. All of the samples showed typical diode behavior. As previously described, the solar conversion efficiency is at the point of maximum power under the I-V curve between the short-circuit current and open-circuit voltage points. The efficiency and fill factor as a function of QWR layers are presented in Figure 26.

For the reference sample (no QWRs), the efficiency was 2.3%, with a fill factor of 0.45. For the QWR samples, with 3, 5, 10, 15, 20 layers of QWRs, the efficiencies were 2.1%, 2.9%, 3.7%, 3.3%, 3.9%, and 3.3%, with fill factors of 0.55, 0.58, 0.58, 0.53, 0.63, and 0.52, respectively. The solar conversion efficiency for all the QWR samples was higher than the reference cell, with 15 layers of QWRs producing the highest efficiency and fill factor.
Figure 25. Illuminated I-V from the short-circuit current to the open-circuit voltage for the reference p-i-n and structures with 3-20 layers of QWRs.

Figure 26. Solar conversion efficiency and fill factor as a function of number of QWR layers.
4.2.5 Open-Circuit Voltage and Short-Circuit Current

The $V_{oc}$ and $I_{sc}$ as a function of the number of layers of QWRs are shown in Figure 27. The open-circuit voltage increased with the addition of three and five layers of quantum wires and then fell and saturated with the addition of 10, 15, and 20 layers. The sample with three layers of QWRs enhanced the $V_{oc}$ by 40 mV and the sample with five layers enhanced the $V_{oc}$ by 160 mV.

All of the QWR samples showed a larger $V_{oc}$ than the reference sample and, with the exception of the sample with three layers of QWRs, showed a larger $I_{sc}$ than the reference. In previously published QD IBSCs, the open-circuit voltage of the QD samples was smaller than their reference. The increase in $I_{sc}$ in the QWR samples was due to photons with energies lower than the GaAs band gap exciting electronic transitions in the QWRs.

**Figure 27.** Short-circuit current and open-circuit voltage as a function of number of QWR layers.
4.2.6 Outcome

The results of this investigation show the relationship between the number of quantum wire layers and the external quantum efficiency and transmission. As expected, the external quantum efficiency of the quantum wires increased with an increase in the number of quantum wire layers. This investigation showed the energy levels of the quantum wires. These results also demonstrated the increase in solar conversion efficiency of the quantum wire structures due to the increase in photo-current from the absorption of photons with energies below the GaAs band gap. Also, the absorption spectrum was broadened due to the presence of the quantum wires, as expected.

4.3 Increasing Absorption in the Space-Charge Region

In the previous structures, most of the solar spectrum at energies above the GaAs band gap energy is absorbed in the top p-type layer, where it does not contribute to the solar conversion efficiency. So the solar cell structure was changed to allow more light to be absorbed in the space-charge region. A thin AlGaAs window layer was inserted on top of the device to couple more light into the device. The window layer reduced reflection by lowering the index of refraction difference between air and the device from 3.3 to 2.9. Then, the p-type emitter region was thinned to limit absorption in the quasi-neutral region. Also, the p- and n-type doping levels were increased to create a stronger internal electric field. An n$^+$-doped substrate was used with back-side metallization to decrease the internal resistance.

4.3.1 Fabrication Mask Considerations
For semiconductor solar cells, metal electrode contacts are fabricated on the top layer (emitter), where the sunlight impinges on the device. The dimensions of these metal contacts have a substantial impact on the efficiency of the solar cell. The two main factors that contribute to the loss of efficiency are shadowing from the metal and resistance due to lateral flow of current between the fingers of the electrodes. Shadowing is simply expressed as a percentage of the area of the metal to area of the whole collection region, and results in a reduction of the solar power seen by the collection region. The power loss due to the lateral resistance is expressed as

\[ P = j^2 l R \frac{d^3}{24} \]  

(Equation 4.3)

where \( j \) is the photocurrent density, \( l \) is the width of the metal fingers, \( R \) is the metal-semiconductor resistance, and \( d \) is the separation between each finger [56]. Therefore, minimizing the width of the separation of the contact fingers is crucial to mitigating power loss. However, this increases the number of fingers, thereby increasing the shadowing.

The photolithography fabrication facilities at the University of Arkansas are capable of alignment precision of 2 µm. However, for a successful liftoff process, the features should be at least 20 µm. With these parameters in mind, the mask for the high-efficiency solar cells was designed with a finger width of 30 µm and finger separation of 403 µm, corresponding to an overall shadowing loss of approximately 20% and a lateral resistance power loss of 1.3 mW/cm². The mask design corresponding to these parameters is shown in Figure 28.

4.3.2 Current-Voltage

Using the same methods as described previously, the current response of the samples to an applied voltage was measured in dark conditions and under solar simulated illumination from 82 to 300 K. The results are shown in Figure 29.
Figure 28. Optimized photolithography masks. (a) Solar cell mesa-etch photolithography mask. (b) solar cell emitter metal-contact photolithography mask.

Figure 29. Dark I-V for samples SF130 and SF136.

Both samples showed a strong deviation from the ideal diode behavior with an ideality factor greater than 2.7. This strongly indicates the presence of SRH and Auger recombinations. From $0.2 < V < 0.6$, the reference and QWR cell showed an ideality factor above $n = 2.7$ at 300
K. This was likely due to the higher electric field in the depletion region from the higher doping densities in both the n- and p-type regions causing SRH and Auger recombination effects.

As shown in Figure 30, the reference cell (without QWRs) shows typical diode behavior. The QWR sample showed a strong anomalous behavior that deviated strongly from an ideal diode, especially in the negative current region of the forward bias. The reference solar cell exhibited a solar conversion efficiency of 11.9%, while the QWR cell exhibited an efficiency of 6.7%. It should be noted, that the I-V characteristics of the QWR cell above 0.75 V showed a better potential for a solar cell. But, where the maximum solar power is generated is where the anomalous behavior was most pronounced. More work is needed to understand if this behavior can be corrected by engineering the QWR IB differently.

Figure 30. Dark and illuminated I-V for samples SF130 and SF136.
4.3.3 Outcome

This investigation showed an increase of solar conversion efficiency for the reference solar cell as more light was absorbed in the space-charge region due to the window layer and thinner emitter layer. Additionally, the quantum wire solar cell showed a decrease in solar conversion efficiency compared to its reference, but an increase in efficiency compared to the previously discussed quantum wire solar cells. This investigation demonstrated that effective design of the solar cell structure could be implemented to increase the solar flux impinging on the space-charge region to enhance the overall photocurrent.

4.4 Effect of Increasing the Space-Charge Field on the Intermediate Band

4.4.1 External Quantum Efficiency

The external quantum efficiency was measured in the same manner as described in previous experiments and is shown in Figure 31. The peak EQE for the reference GaAs cell was 78.86%. For the QWR cell, the GaAs EQE peak was higher than the reference at 82.92%. The EQE peak from the QWRs showed a decrease from previous samples at 6.8%. The QWR cell showed a higher EQE response from wavelengths of 500 nm to 1000 nm (~4% higher in the GaAs and 6.8% higher in the QWRs). It is unknown why the QWR sample showed a higher EQE in the GaAs region above 500 nm.

The device current due to Shockley-Read-Hall (SRH) effects arises from trap-assisted recombination events in the depletion region of the diode under low-level injection. These types of events are most likely to occur at surfaces and interfaces where a large number of electrically active states exist due to the abrupt change or termination in the crystal lattice. The magnitude of the SRH current depends mainly on the applied voltage.
To investigate the existence of trap-assisted recombination, the samples were biased by an externally applied voltage (in increments of 100 mV) and the EQE spectrum was measured from 300 nm to 1100 nm and is shown in Figure 32. It is clear that the reference cell EQE degradation was minimal (less than 5%) in the bulk GaAs region, up to 700 mV. However, the QWR sample’s EQE was already degraded by ~20% in the GaAs region and ~50% in the QWRs at 500 mV. At 700 mV, the EQE of the bulk GaAs region was degraded by ~75% in the QWR sample.
Figure 32. External quantum efficiency with applied forward bias 0-700mV for SF130 (Ref.) and SF136 (QWRs).

4.4.2 Outcome

This investigation demonstrated an increase in the external quantum efficiency in the quantum wires compared to the reference. However, this increase was not as large as expected compared to previous samples. This investigation also showed that the forward bias external quantum efficiency was degraded by the quantum wires acting as traps. Furthermore, the quantum wires structure showed an increase in short-circuit current compared to the reference; but this increase was not as much as expected due to the behavior of the quantum wires as possible trap states for the electrons.

4.5 Temperature Effects on the Intermediate Band

4.5.1 Solar Conversion Efficiency

Studies of solar conversion efficiency as a function of temperature were performed for each sample. The temperature dependence of these structures was important to investigate
because the absorption changes as a function of temperature due to the change in electrons populating the intermediate band. Variable temperature measurements of solar efficiency were performed using a cryostat from MMR Technologies [57] under vacuum. The efficiency as a function of decreasing temperature is shown in Figure 33.

The general trend for all of the samples was an increase in efficiency as the temperature was decreased from 300 to 180 K showing a linear dependence. In the temperature range from 165 to 180 K, there was a dramatic change in the functional dependence on temperature of the samples. Below 180 K, the reference efficiency slope flattened, with only a slight increase as

![Figure 33. Solar conversion efficiency as a function of temperature for samples SE159-SE165.](image-url)
temperature decreases. Below 165 K, the efficiency of the undoped QWRs increased sharply, only to decrease again at lower temperatures. Below 165 K, the efficiency of the δ-doped samples tended to flatten, with the mid-level δ-doped sample showing a decreasing trend throughout the remaining temperature range.

The temperature dependent solar conversion efficiency of the optimized solar cell structure is shown in Figure 34. Unlike the previous samples, the reference cell had a minimal drop in efficiency below 180 K of less than 1%. However, the slope of the efficiency changed due to the degradation of the short-circuit current. The QWR sample showed no discernible drop in efficiency below 180 K, but the slope did saturate.

![Figure 34. Solar conversion efficiency as a function of temperature for samples SF130 (Ref.) and SF136 (QWRs).](image)
4.5.2 Open-Circuit Voltage and Short-Circuit Current

The open-circuit voltage point occurs when the measured current is equal to zero. This occurs when the diode current equals the light-generated current. The open-circuit voltage as a function of temperature, from 300 to 82 K, is shown in Figure 35.

![Figure 35. Open-circuit voltage as a function of temperature for samples SE159-SE165.](image)

The temperature dependence of the open circuit voltage is given by:

\[
V_{oc} = \frac{E_g}{q} - \frac{AkT}{q} \ln \left( \frac{I_{00}}{I_L} \right)
\]

(Equation 4.4)

where \(E_g\) is the material band gap energy, and \(I_{00}\) is the dark saturation current due to recombination in the quasi-neutral regions. However, the main component that attributes to the change in \(V_{oc}\) as a function of temperature is the band gap because the dark saturation current is
small compared to the photo-current. Over the temperature range from 300 to 82 K, the increase in the GaAs band gap is approximately linear.

The short-circuit current is the current through the solar cell when the voltage across the device is zero. The short-circuit current is produced by the photo-generation of carriers. The short-circuit current is the highest magnitude of current that can be drawn from the device. The components of the short circuit current that depend on temperature are the generation rate and the minority carrier diffusion lengths, which depend on their lifetimes. The short-circuit current as a function of temperature for samples SE159 – SE165 is shown in Figure 36.

![Figure 36. Short-circuit current as a function of temperature for samples SE159-SE165.](image-url)
In GaAs, as the temperature decreases, the lifetimes increase, which resulted in an increase in $I_{sc}$ to ~180 K. Below 180 K, the δ-doped samples showed a decrease in $I_{sc}$ due to freezing of the free electrons in the IB [58]. This has the effect of filling the IB states and thereby reducing the optical absorption.

For samples SF130 (reference) and SF136 (QWRs), the I-V response was measured as a function of temperature, from 300 to 82 K. The temperature dependent open-circuit voltage is shown in Figure 37. For both the reference and QWR samples, $V_{oc}$ showed a linear increase as a function of decreasing temperature. The open-circuit voltage mainly depends on the effective material band gap, which is approximately linear in this temperature range.

![Figure 37. Open-circuit voltage as a function of temperature for samples SF130 (Ref.) and SF136 (QWRs).](image)
However, the QWR sample showed a substantial drop in $V_{oc}$, much larger than in previous results. The open-circuit voltage of the reference cell was 0.91 V, while the QWR cell was 0.73 V. The position of the QWRs in this solar cell structure was no longer symmetrically located, with respect to the space-charge region. Because of the asymmetric design of the solar cell, the QWRs were shifted toward the emitter. An investigation on the effect of the location of QDs in solar cells by Driscoll et al. showed that emitter-shifted QDs in the presence of a high electric field resulted in a substantially reduced $V_{oc}$ and solar efficiency [33].

The temperature dependent short-circuit current is shown in Figure 38. The QWR sample showed a higher $I_{sc}$ of 6.15 mA compared to the reference cells $I_{sc}$ of 6.0 mA. Both samples showed the same characteristic drop in $I_{sc}$ below 180 K as seen in previous results.

Figure 38. Short-circuit current as a function of temperature for samples SF130 (Ref.) and SF136 (QWRs).
4.5.3 Outcome

While the sensitivity to temperature for the quantum wire intermediate band solar cell was not improved, it was demonstrated that adding the intermediate levels did not increase the sensitivity above that of the reference cell. In addition, the results of this section demonstrate that decreasing temperature increased the solar conversion efficiency. This increase was due to an increase in open-circuit voltage and short-circuit current as temperature decreased until carriers were frozen out of the conduction process. At room temperature, the solar conversion efficiency changes less than 5.7% for a ±10 K change in temperature.

4.6 Detailed Discussion on Each of the Three Sets of Samples

4.6.1 δ-doped Solar Cell Structure

Using an MBE 32P Riber system, seven samples were grown, in the following order: (1) p-n diode with a 400 nm GaAs buffer, then a 1 µm n-type \((N_D = 5.0 \times 10^{17} \text{ cm}^{-3})\) GaAs region, then a 1 µm p-type \((N_A = 5.0 \times 10^{17} \text{ cm}^{-3})\) GaAs region (SE159); (2) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then 10 layers of In\(_{40}\)Ga\(_{60}\)As QWRs separated by a 30 nm GaAs spacer, then a 1 µm p-type GaAs region (SE160); (3) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then 10 layers of In\(_{40}\)Ga\(_{60}\)As QWRs separated by a 30 nm GaAs spacer with δ-doping in the middle of the spacer region \((N_D = 6.7 \times 10^{10} \text{ cm}^{-2})\), then a 1 µm p-type GaAs region (SE161); (4) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then 10 layers of In\(_{40}\)Ga\(_{60}\)As QWRs separated by a 30 nm GaAs spacer with δ-doping in the middle of the spacer region \((N_D = 1.0 \times 10^{11} \text{ cm}^{-2})\), then a 1 µm p-type GaAs region (SE162); (5) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then 10 layers of In\(_{40}\)Ga\(_{60}\)As QWRs separated by a 30 nm GaAs spacer with δ-doping in the middle of the spacer region.
region \( (N_D = 5 \times 10^{11} \text{ cm}^{-2}) \), then a 1 µm p-type GaAs region \( \text{(SE163)} \); (6) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then a 330 nm intrinsic GaAs region, then a 1 µm p-type GaAs region \( \text{(SE164)} \); (7) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then 10 layers of 30 nm GaAs spacers with δ-doping in the middle of the spacer region \( (N_D = 1.0 \times 10^{11} \text{ cm}^{-2}) \), then a 1 µm p-type GaAs region \( \text{(SE165)} \). The sample structures are shown in Figure 39.

**Figure 39.** Example of solar cell structures for δ-doped sample series.

All samples were fabricated as 5 mm x 5 mm solar cells using standard photolithography techniques and wet chemical etching. Ohmic contacts were prepared using AuGe/Ni/Au and AuZn/Au for the n- and p-type GaAs layers, respectively, using e-beam evaporation. The metals
were alloyed by annealing at 420 °C for the n-type metal contact and 300 °C for the p-type contact in an atmosphere of dry nitrogen.

4.6.2 Multiple QWR Layers Solar Cell Structure

In addition to doping the intermediate energy levels, it also had to be determined how many layers of quantum wires could be added since this directly controls the absorption of solar light. Six samples were grown, using an MBE 32P Riber system, to examine this question, and is shown in Figure 40.

![Diagram of solar cell structure](image)

**Figure 40.** Solar cell structure for varying QWR layer series.

These structures were grown in the following manner: (1) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type \( N_D = 5.0 \times 10^{17} \text{ cm}^{-3} \) GaAs region, then a 420 nm GaAs intrinsic
layer, then a 1 µm p-type \((N_A = 5.0 \times 10^{17} \text{ cm}^{-3})\) GaAs region (SE239); (2) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then a 20 nm spacer layer, then 20 layers of In\textsubscript{40}Ga\textsubscript{60}As QWRs separated by a 20 nm GaAs spacer, then a 1 µm p-type GaAs region (SE240); (3) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then a 120 nm spacer layer, then 10 layers of In\textsubscript{40}Ga\textsubscript{60}As QWRs separated by a 20 nm GaAs spacer, then a 120 nm spacer layer, then a 1 µm p-type GaAs region (SE241); (4) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then a 190 nm spacer layer, then 3 layers of In\textsubscript{40}Ga\textsubscript{60}As QWRs separated by a 20 nm GaAs spacer, then a 190 nm spacer layer, then a 1 µm p-type GaAs region (SE242); (5) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then a 170 nm spacer layer, then 5 layers of In\textsubscript{40}Ga\textsubscript{60}As QWRs separated by a 20 nm GaAs spacer, then a 170 nm spacer layer, then a 1 µm p-type GaAs region (SE243); (6) p-i-n with a 400 nm GaAs buffer, then a 1 µm n-type GaAs region, then a 70 nm spacer layer, then 15 layers of In\textsubscript{40}Ga\textsubscript{60}As QWRs separated by a 20 nm GaAs spacer, then a 70 nm spacer layer, then a 1 µm p-type GaAs region (SE245).

All samples were fabricated as 5 mm x 5 mm solar cells using standard photolithography techniques and wet chemical etching. Ohmic contacts were prepared using AuGe/Ni/Au and AuZn/Au for the n- and p-type GaAs layers, respectively, using e-beam evaporation. The metals were alloyed by annealing at 420 °C for the n-type metal contact and 300 °C for the p-type contact in an atmosphere of dry nitrogen.

**4.6.3 Increased Absorption to the Space-Charge Region Solar Cell Structure**

Another aspect of the intermediate band solar cell to investigate was the control of absorption in the space charge region. To investigate this possibility, two different structures were grown by MBE and then fabricated and processed identically to see which cell had the
highest efficiency produced by our facilities. The structure that produced the highest solar conversion efficiency at room temperature was the structure in reference 18. For the high efficiency solar cell, silicon p-type doping was not a viable option because the maximum effective hole concentration was less than $10^{18}$ cm$^{-3}$.

Using an MBE 32P Riber system, two different samples were grown. A schematic diagram of the material structure of the solar cell devices is presented in Figure 41.

**Figure 41.** Solar cell structure for enhancing the optical penetration and electric field in the space-charge region.

First, a reference GaAs high efficiency solar cell was grown (SF130). A 250 nm GaAs n-type (Si) doped ($N_D = 1 \times 10^{18}$ cm$^{-3}$) buffer layer was grown on the n-type doped GaAs (311)A surface at 525 °C. In order to obtain high n-type doping efficiency for the GaAs layer on the (311)A surface, a low growth temperature and high V/III flux ratio ($V/III = 20$) were used. Then,
a 3 µm n-type \( (N_D = 8 \times 10^{16} \text{ cm}^{-3}) \) base was grown at the same temperature. Using the same growth temperature, a 330 nm thick GaAs intrinsic region was grown. The temperature was increased to 580 °C and a 400 nm GaAs p-type (Be) doped \( (N_D = 1 \times 10^{18} \text{ cm}^{-3}) \) region was grown, followed by a 30 nm \( \text{Al}_{0.8}\text{Ga}_{0.2}\text{As} \) p-type doped \( (N_D = 1 \times 10^{18} \text{ cm}^{-3}) \) window layer and 10 nm GaAs p-type \( (N_D = 5 \times 10^{18} \text{ cm}^{-3}) \) capping layer. For the high-efficiency IB-QWR-SC, this growth was repeated two more times with same parameters with the intermediate band grown in the GaAs-i-region, which contained 10 periods of 11 monolayers of \( \text{In}_{0.4}\text{Ga}_{0.6}\text{As} \) QWRs, separated by 30 nm barriers, for SF136.

The samples were processed as solar cell devices using standard optical photolithography of a high-efficiency solar mask and wet chemical etching into 5 mm x 5 mm square devices. For n-type and p-type contacts, \( \text{AuGe}/\text{Ni}/\text{Au} \) and \( \text{AuZn}/\text{Au} \) metallizations were applied, respectively. High-quality ohmic contacts were obtained by rapid thermal annealing at 470 °C for n-type (bottom contact) and 350 °C for p-type (top contact).
Chapter 5: Conclusion

The first goal of this research was to develop the first quantum wire intermediate band solar cell. This was achieved by MBE growth of InGaAs self-assembled quantum wires imbedded in a GaAs p-i-n diode. Cross-sectional TEM showed that the QWR structure was free of strain-related defects.

The second goal was to demonstrate that the solar efficiency of the QWR cell is higher than the reference cell. The quantum wire intermediate band solar cell structures grown for this research produced a higher solar conversion efficiency than its reference cell. This was the first reported IBSC with an increase in efficiency. The QWR IBSC showed an increase in efficiency of 13.3% over the reference, and the lowest reduction in open-circuit voltage (20mV) [54]. The efficiency increase was due to photocurrent generation from the absorption of sub-band gap energy photons by the quantum wires. It is believed the quantum wire intermediate band solar cell performed better than similar quantum dot structures due to (a) the significantly larger density of states of the QWRs and higher spatial density increasing the absorption of normal incident light and (b) the lateral transport for photo-generated carriers.

Having demonstrated the first quantum wire intermediate band solar cell and enhanced absorption of the solar spectrum into the infrared over a reference cell without quantum wires, ways to understand the undying physics and increase the solar efficiency were investigated. These efforts were focused on increasing the absorption of the quantum wires by doping of the intermediate band. While the incorporation of δ-doping to partially fill the intermediate band did not result in increasing the amplitude of the quantum efficiency of the QWRs, this did result in an increase in the photocurrent and suppressed recombination effects of the QWRs in the space-
charge region. In addition, at low $\delta$-doping, an increase in the lifetime of electrons in the ground state of the QWRs was observed.

To further optimize the operation of the QWR IB, the number of quantum wire layers comprising the intermediate band was varied and their behavior was characterized. The increase in the number of QWR layers enhanced the absorption of the intermediate band and the quantum efficiency monotonically increased with an increase in the number of layers at photon energies below the GaAs band gap energy. The photocurrent of the solar cell was enhanced by adding more layers of QWRs and exhibits voltage preservation.

This research showed the importance of fine tuning the solar cell device structure. For example, by creating a window layer and thinning the p-type emitter layer, the absorption of the solar cell was enhanced substantially, as indicated by the increase in peak quantum efficiency, especially in the visible wavelength range, where the peak of the solar spectrum lies. The increase in absorption and enhancement of the internal space-charge field improved the photocurrent substantially, by more than a factor of two compared to previous structures, for both the reference and QWR cells. However, the enhancement of the electric field and lack of doping led to the quantum wires behaving as recombination sites for the photo-generated electrons through Shockley-Read-Hall and possible Auger recombination due to the non-ideal diode behavior.

Finally, by adding quantum wires, the possibility existed that these structures might negatively impact the solar cell performance under variation in temperature. Fortunately, it was demonstrated that adding the intermediate band did not increase the sensitivity of the solar cell to temperature above that of the reference cell, and the quantum wires introduced no negative effects on sensitivity to temperature variation.

In summary, the first quantum wire intermediate band solar cell was successfully developed. The quantum wire intermediate band solar cell had a clear improvement in
performance over a reference cell due to increased absorption of the solar spectrum in the infrared region.
Chapter 6: Future Work

The results of the research presented here is the beginning of what could be a huge field of potential research areas. There are still many unanswered questions about the effect of doping the intermediate band. While δ-doping was used in this research, other types, methods, and levels of doping should be explored to optimize the absorption process in the intermediate band process.

One major area of improvement and future research lies in the modeling of QWRs in p-i-n diode structures to simulate their behavior. A robust and complete simulation would allow for optimizing of QWR solar cells to understand how many of the parameters (position, periods, doping, height, etc) affect the band structure and I-V characteristics. Therefore, growth structures could be optimized and compared to the model to gain more understanding of the device physics.

One very interesting field that is yet to be explored is the engineering of the piezoelectric field for solar cell applications. Lattice-mismatch-induced-strain in GaAs (111) has been shown to produce internal piezoelectric fields in excess of 100kV/cm [59]. It is expected that internal piezoelectric fields can be produced in GaAs (311)A. This internal piezoelectric field could be engineered to enhance the extraction of photo-generated electrons/holes by adding to the internal space-charge field, especially for quantum dot and quantum wire based solar cells.

As with all strained-epitaxy based structures, the strain accumulates through the material and can result in strain-related dislocations and other defects. In many QD-based electronic structures, strain-relieving layers (typically GaP) are placed in the barriers to prevent or reduce defects and allow for the QD layers to be in close proximity to enhance coupling. This concept can be extended to QWR-based solar cells for the same reason.
References


[34] V. Popescu, G. Bester, M. C. Hanna, A. G. Norman, and A. Zunger, “Theoretical and experimental examination of the intermediate-band concept for strain-balanced


Appendix A: Description of Research for Popular Publication

Quantum Wire Intermediate-Band Boosts Solar Cell Efficiency

By Colin Furrow

Researchers at the University of Arkansas in Dr. Salamo’s Nanotechnology group are using nanostructures to create the next generation of solar cells. Remarkably, the concept they are exploring works by reducing the complexity of high-efficiency solar cells. The current high-efficiency solar cells (triple-junction cells) work by layering three different solar cells together in a tandem configuration. This allows for different parts of the solar spectrum to be absorbed and converted into electrical current. The problem is that these solar cells are very expensive and complex to manufacture and only result in efficiencies of around 30%.

Dr. Salamo’s PhD candidate, Colin Furrow, explains there is an alternative to triple junctions to reach high efficiencies by using an intermediate band. “Solar cells only absorb a fraction of the solar spectrum and most of the infrared light just passes through.” So the intermediate band was proposed as a way of capturing the lower energy light. Dr. Salamo’s group is growing quantum wires (nanowires) in the middle of a standard GaAs solar cell. These quantum wires are only four nanometers tall, so small that traditional optical imaging is impossible. Special microscopes using electrons or atomically sharp tips allow the researches to view these nanostructures. These structures are carefully grown by a process called Molecular Beam Epitaxy (MBE). By using MBE, the researchers can grow new materials one atomic layer at a time, free of impurities.
By using just 10 layers of these quantum wires, this new solar cell technology produces a 13.3% percent efficiency increase over the standard solar cell. As Dr. Salamo explains, “The nanostructures comprise less than 1% of the material in the solar cell, but they substantially improve the efficiency.” This research is just the beginning to understanding the device physics of how these structures operate in the solar cell. Salamo’s group is trying to optimize the behavior of the quantum wires. They believe they can further enhance the absorption of these structures by adding more layers of quantum wires and providing more electrons to the intermediate band.

Dr. Salamo’s group hopes that their research will lead to a new direction in solar cell development. This promising concept is just the first step in finding new solar cell materials that are less complex and yield higher efficiencies. They hope that these will become a cost effective alternative to the current state of the art triple-junction solar cells.
Appendix B: Executive Summary of Newly Created Intellectual Property

The following list of new intellectual property items were created in the course of this research project and should be considered from both a patent and commercialization perspective.

1. This research produced the first solar InGaAs quantum wire solar cell.

2. This research produced the first quantum wire intermediate band solar cell.

3. This research produced the first intermediate band solar cell to show a higher efficiency than the reference solar cell and a reduction of open-circuit voltage of only 20mV (lowest reported at the time of publication).
Appendix C: Potential Patent and Commercialization Aspects of listed Intellectual Property Items

C.1 Patentability of Intellectual Property (Could Each Item be Patented)

The three items listed were considered first from the perspective of whether or not the item could be patented.

1. The concept of a quantum wire solar cell by atomic layer deposition was patented in US Patent: US 20100240167 A1. This patent covers self-assembled and nano-patterned deposition techniques, where the nanostructures are placed in the intrinsic region of a p-i-n diode, and specifically addresses intermediate bandgaps and multiple-exciton producing devices.

2. The concepts described in US Patents: WO2012009808 A1 and US8378209 B2 are similar to the previously listed patent, with the latter having an emphasis on concentrated solar cells.

3. The “Intermediate band semiconductor photovoltaic solar cell”, US Patent: US6444897 B1, was patented in 2000 by Luque et al., who developed much of the concepts used to produce this research.

The intellectual property in the above listed patents address concepts that overlap with the intellectual property discussed in this research.
C.2 Commercialization Prospects (Should Each Item Be Patented)

The three items listed were then considered from the perspective of whether or not the item should be patented.

Due to the patents discussed in the previous section, a patent on the intellectual property created by this research should not be pursued.

C.3 Possible Prior Disclosure of IP

The following items were discussed in a public forum or have published information that could impact the patentability of the listed IP.

1. All of the details of this research were discussed in group meetings and presented at the Arkansas Space Grant Consortium and the VICTER Conference.

2. The results of this research were published in two peer-reviewed journal articles and another draft is planned for publication.
Appendix D: Broader Impact of Research

D.1 Applicability of Research Methods to Other Problems

The research methods described in this research can be applied to the development of new material systems for a wide variety of applications, where material, optical, and electrical characterization is required. While the concept of the intermediate band was developed with a focus on solar cells, this idea could be extended to devices that function similar to solar cells, such as infrared photodetectors and photoresistors. Additionally, there is a growing interest in the possibility of using InGaAs quantum wires in thermoelectric devices. Development of these devices would require similar characterization described in this research. The growth methodology pertaining to this research can be extended to other III-V semiconductor materials (nitrides, phosphides, antimonides, bismides), as well as some II-VI materials and possibly oxides, especially those grown by MBE.

D.2 Impact of Research Results on U.S. and Global Society

The results of this research are still very preliminary in the development of a possible commercially viable process. However, the growth of quantum wires could be implemented in commercial MBE-grown GaAs solar cells in the very near future. Currently, self-assembled QWRs have not been observed by MOCVD growth, but if this can be achieved, it represents the best cost-effective opportunity for a commercial quantum wire intermediate-band solar cell.
D.3 Impact of Research Results on the Environment

The short-term impact of this research is the use and by-products of hazardous materials used in creating the device structures, such as arsenic, phosphoric acid, etc. The arsenic used as the base material for these solar cells is toxic and has to be handled and disposed of according to EPA regulations. The long-term impact of this research could result in an alternative energy source (solar) that reduces the reliance on coal and gas based energy sources, thereby reducing atmospheric pollutants and greenhouse gases. Of course, the by-product of arsenic and other hazardous materials would still exist.
Appendix E: Microsoft Project for MS MicroEP Degree Plan
Appendix F: Identification of All Software Used in Research and Dissertation Generation

Computer #1:
  Model Number: DELL OPTIPLEX 760
  Serial Number: N/A
  Location: PHYS 239
  Owner: University of Arkansas

Software #1:
  Name: Microsoft Office 2007 Suite
  Purchased by: Greg Salamo

Software #2:
  Name: OriginLab OriginPro 8
  Purchased by: Greg Salamo (Group License)

Software #3:
  Name: Microsoft Project 2010
  Purchased by: Colin Furrow

Computer #2:
  Model Number: DELL OPTIPLEX Gn
  Serial Number: 7027049
  Location: NANO 152
  Owner: University of Arkansas

Software #1:
  Name: Metrics
  Purchased by: Greg Salamo

Software #2:
  Name: MMR K-20 Temperature Controller
  Purchased by: Greg Salamo

Computer #3:
  Model Number: Lenovo IdeaPad G510
  Serial Number: N/A
  Location: Home
  Owner: Colin Furrow

Software #1:
  Name: Microsoft Office 2013 Suite
  Purchased by: Colin Furrow
Appendix G: All Publications Published, Submitted and Planned


