ABSTRACT

SAMBERG, JOSHUA PAUL. Multi-Quantum Well Structures to Improve the Performance of Multijunction Solar Cells. (Under the direction of Dr. Nadia El-Masry and Dr. Salah Bedair.)

Current, lattice matched triple junction solar cell efficiency is approximately 44% at a solar concentration of 942×. Higher efficiency for such cells can be realized with the development of a 1eV bandgap material lattice matched to Ge. One of the more promising materials for this application is that of the InGaAs/GaAsP multi-quantum well (MQW) structure. By inserting a stress/strain-balanced InGaAs/GaAsP MQW structure into the i-region of a GaAs p-i-n diode, the absorption edge of the p-i-n diode can be red shifted with respect to that of a standard GaAs p-n diode. Compressive stress in the InGaAs wells are balanced via GaAsP barriers subjected to tensile stress. Individually, the InGaAs and GaAsP layers are grown below their critical layer thickness to prevent the formation of misfit and threading dislocations.

Until recently InGaAs/GaAsP MQWs have been somewhat hindered by their usage of low phosphorus-GaAsP barriers. Presented within is the development of a high-P composition GaAsP and the merits for using such a high composition of phosphorus are discussed. It is believed that these barriers represent the highest phosphorus content to date in such a structure. By using high composition GaAsP the carriers are collected via tunneling (for barriers ≤30Å) as opposed to thermionic emission. Thus, by utilizing thin, high content GaAsP barriers one can increase the percentage of the intrinsic region in a p-i-n structure that is comprised of the InGaAs well in addition to increasing the number of periods that can be grown for a given depletion width. However, standard MQWs of this type inherently possess undesirable compressive strain and quantum size effects (QSE) that cause the optical absorption of the InGaAs wells to blue shift. To circumvent these deleterious QSEs stress balanced, pseudomorphic InGaAs/GaAsP staggered MQWs were developed. Tunneling is still a viable mode for carrier transport in the staggered MQW structures.

GaAs interfacial layers within the multi-quantum well have been found to be critical in producing quality multi-quantum well structures. The effect of the GaAs interfacial layers has been investigated. It was determined that a phosphorus carry-over had a profound effect
on the absorption edge of the InGaAs wells. It was shown that the phosphorus carry-over can be prevented with sufficiently thick GaAs transition layers. Preliminary results for GaAs p-i-n solar cells utilizing the improved MQWs are presented.

In addition to investigating the utilization of quantum wells in the i-region of a GaAs p-i-n diode to improve the efficiency of multijunction solar cells, an investigation into the effect a single GaAs:Te doped quantum well has on the performance of high bandgap In$_x$Ga$_{1-x}$P:Te/Al$_{0.6}$Ga$_{0.4}$As:C tunnel junctions was investigated. The insertion of 30Å of GaAs:Te at the junction interface resulted in a peak current of 1000A/cm$^2$ and a voltage drop of ~3mV for 30A/cm$^2$ (2000× concentration). The presence of this GaAs interfacial layer also improved the uniformity across the wafer. This architecture could be used within multijunction solar cells to extend the range of usable solar concentration with minimal voltage drop.
Multi-Quantum Well Structures to Improve the Performance of Multijunction Solar Cells

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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DEDICATION

I would like to dedicate this dissertation to my loving family.
BIOGRAPHY

Joshua Samberg was born on Elmendorf Air Force Base, located just outside of Anchorage, Alaska. At the age of five, Josh and his family were relocated to Fort Benning, Georgia. He grew up on a small, family farm in rural Georgia helping to foster his love of science and engineering. Eventually, he would attend the University of Georgia to pursue a Bachelors of Science degree in Chemistry. Upon graduating summa cum laude from the University of Georgia, Joshua had his sights on attending Medical School. However, the lingering feeling of leaving engineering proved too much. This love of engineering ultimately led to the pursuit of a Doctorate of Philosophy in Materials Science and Engineering.
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CHAPTER 1: Energy

1.1 Introduction

Throughout much of history the main energy resources for humans were renewable. Wood was burned to heat homes and cook while the power of water and wind was harnessed to run mills and factories. These renewable energies produce a net zero carbon footprint, the total set of greenhouse gas (GHG) emissions. The technological revolution brought with it the proliferative usage of fossil fuels such as coal, petroleum and natural gas. There is scientific evidence that suggests the burning of these fossil fuels for the last 160 years is contributing to the observed current global climate change.\(^1\)\(^2\) Carbon dioxide and methane atmospheric, greenhouse gas levels are now at 400 parts per million (PPM)\(^3\) and 1800 parts per billion (PPB)\(^4\), respectively. While there is some debate as to how much humans have actually contributed to this increase in greenhouse gas levels, whether wholly or in part, there is little debate to what must be done to assuage the contribution by humanity. Transitioning away from fossil fuels to more environmentally responsible renewable energies will greatly reduce the carbon footprint. It is the ultimate goal of the research herein to facilitate a society independent of fossil fuels.

1.2 Future Energy

When analyzing world energy consumption and endeavoring to forecast future energy needs, several questions arise: What do the global energy reserves for fossil fuels look like? How much energy will future generations need? Which renewable energy technologies are viable alternatives? At what point will these alternative technologies become economically competitive with fossil fuels? While these questions are difficult to answer, what follows is an attempt to answer them utilizing the latest data available. Furthermore, when dealing with the energy reserves for fossil fuels it is imperative to view them individually as they play very different rolls in supplying energy. Additionally, the values reported are for proven reserves, reservoirs of coal seams, oil and natural gas that companies are confident are profitable for development using current extraction technologies. That being said, these values are subject to change as new extraction technologies are developed.
Coal is the most abundant fossil fuel on the planet and is found mostly in politically stable countries, allowing for reliable reserve values. In most countries coal is used to fire the primary power generation stations. These generation stations provide constant power, also termed basic load, to the grid but not the additional power needed during peak hours. According to the U.S. Energy Information Administration (EIA) in 2010, the estimated recoverable coal reserves are around 948 short tons (1 short ton=2000 lbs.) and would last approximately 222 years.\(^5\)

Both natural gas and oil are used in powering the secondary power generation stations, the additional power needed during peak demand, and oil is also the primary energy source for transportation. Reserves of natural gas are estimated around 6675 trillion cubic feet by the EIA.\(^6\) Natural gas is the fastest growing fossil fuel, primarily due to fracking, and it is expected that a consumption increase of 1.6 percent will occur annually from 2012 to 2035.\(^7\) Even with this growth, it is expected that current reserves of natural gas will last 92 years.\(^8\) The EIA estimates reserves of oil at 1342 billion barrels. At current consumption levels of 80 million barrels a day this reserve will only last 45 years. Recoverable reserves tend to be a bit pessimistic as they assume no other sources for a given resource will be discovered. Regardless of this fact, fossil fuels are a non-renewable energy which can easily be disrupted by a variety of factors such as natural disaster and political unrest. These factors could lead to volatile pricing for such resources in the very near future.

Ultimately, the most important factor in how much energy will be needed in the future is the population. Population estimates range from 6 to 17 billion\(^9\) by the year 2100 with a more conservative estimate by the United Nations of around 11 billion.\(^10\) With this increase in population, along with the industrialization of more countries, it is likely the energy demand per capita will continue to increase. However, there are technologies that could help alleviate the increase in energy demand such as LED lighting,\(^11\) Energy Star appliances\(^12\) and SmartGrid technology.\(^13\)

There are a plethora of energy sources which might be available in the future. These sources are classified as either non-renewable or renewable, and can be seen in Table 1-1. Non-renewable energies are derived from resources that cannot be reproduced on a scale
which can sustain its consumption rate while renewable energy resources can. Technically, all energy sources listed in Table 1-1 are solar energies with the exception of radioactive fuel. For the intents and purposes of this dissertation, solar energy will only refer to solar photovoltaic energy. The potential sources for energy will be explored in greater depth in the following sections.

1.2.1 Biofuel

Biofuels are derived from biological carbon fixation and include biogases, liquid biofuels and fuels derived from biomass conversions. Bioethanol and biodiesel currently constitute the largest segment of biofuel and are used primarily in the transportation sector. In 2010, biofuel production was approximately 700 million barrels and provided 2.7% of the world's transportation fuel. The International Energy Agency (IEA) predicts that biofuels have the potential to supply 27% of the world’s energy fuel demands by 2050.

1.2.2 Biomass

Similar to biofuel and often used as its precursor, biomass is a fuel created by carbon fixation in organisms. In its more general form, biomass is plant matter which can be burned to generate electricity. Biomass systems utilize scrubbers similar to that found on fossil fuel systems. These scrubbers clean the air exiting the power plants while the growing crops withdraw CO₂ from the atmosphere. Thus, each burning cycle acts like a large cleaning unit for the planet as the crops absorb more CO₂ than is released from the power plant. In 2009, the biomass power generating industry in the United States produced 1.4 percent (11,000 MW) of the U.S. electricity supply.

1.2.3 Geothermal

Geothermal energy is generated and stored in the earth, is derived from the origin of the earth and is augmented by the radioactive decay of elements. Currently, 24 countries utilized geothermal energy in some form, generating about 10715 MW of power. The United States leads the way in total geothermal energy generation producing 3000 MW from 77 power plants. However, this figure only represents 0.3% of total electricity generation. In terms of electricity generation from geothermal energy, Iceland leads the way, producing
around 30% of its total electricity in this manner. However, Iceland is ideally situated on the mid Atlantic ridge, making this form of energy production very feasible. Theoretically, the earth’s geothermal resources are enough to supply humanity’s energy needs. However, it is thought that only a small percentage of this resource can be exploited profitably as drilling and exploration for this deep resource is expensive. Nevertheless, over the past 20 years the generating cost of geothermal power has decreased 25%, primarily due to government assistance and subsidies.\textsuperscript{23}

1.2.4 Hydroelectricity

Hydroelectricity is produced by using the gravitational force of falling water. Globally, hydroelectric power generation is by far the most used form of renewable energy. For some countries, such as Paraguay and Norway, nearly 100% of their electric generation is produced in this manner.\textsuperscript{24} Since 2003, there has been a great increase in the total global electricity production by hydroelectric energy to 3427 TWh in 2010.\textsuperscript{25} The country with the largest hydroelectric generation capabilities is China at a total 721 TWh in 2010.\textsuperscript{25} Additionally, China has started or has plans for 15 more large scale hydroelectric power plants adding potentially 60,000 MW of additional electricity.\textsuperscript{26,27} Hydroelectricity is so widely used because it is cost competitive with fossil fuels. Still, its major detractors relate to the damming of rivers that can harm local ecosystems.

1.2.5 Solar Photovoltaic

Solar photovoltaics (PVs) utilize the photoelectric effect to convert light into an electric current. This is either done directly with solar cell or indirectly after the solar irradiation has been concentrated. There is a range of photovoltaic technologies but for the most part terrestrial solar production is dominated by silicon and thin-film CdTe. PV installation varies greatly with the balance of systems cost being $2.60/Watt in Germany but $4.87/Watt in the United States.\textsuperscript{28} Balance of systems costs include the cost of the PV modules, inverters, wiring, racks, trackers, marketing and permitting. A great deal of work has gone into analyzing the high cost of PV installation in the United States with respect to
the costs in Germany. The basics of how solar photovoltaics work will be discussed in more detail in chapter 2.

1.2.6 Solar Thermal

Solar thermal collectors are classified as low, medium or high temperature collectors. While all these will contribute to a cleaner energy future, the following is restricted to the high temperature collectors as they are utilized in electric power generation. High temperature collectors concentrate the solar irradiance using lenses and mirrors. Currently, solar thermal technologies are more efficient than typical photovoltaic technologies and while only 600MW of solar thermal power was provided worldwide in 2009, current projects will raise this to 14000MW. Additionally, solar thermal power is reliable and can deliver peak power loads. Unfortunately, solar thermal energy is expensive at around $0.25/kWh with an outlook of $0.12/kWh by the year 2020. It does not seem that solar thermal energy will be cost competitive with fossil fuels anytime soon.

1.2.7 Tidal Power

Another type of hydroelectric generation is tidal power. Tidal power harnesses the power of the tides to produce electricity and possesses great potential for future energy generation. The main limitation for tidal power is the availability of sufficient sites. There are three main tidal power generation types: tidal stream generation uses the flow of water to produce electricity, tidal barrage utilizes height differences between high and low tides and dynamic tidal power is a new technology that could be utilized in coastal areas with strong parallel tidal currents. While tidal power constitutes a very small proportion of energy generation worldwide, there are plans to build large generation facilities. Surprisingly, obtaining electricity from tidal power is estimated to be relatively cheap. An 8000MW barrage system proposed in the UK would cost an estimated $15 billion while a 2200 MW tidal fence in the Philippines has been estimated to cost $3 billion. These estimated costs of approximately $2/Watt are similar to installation costs of coal and hydroelectric power station.
1.2.8 Wave Power

Another type of hydroelectric generation is wave power. Wave power utilizes the energy transported in ocean surface waves to generate electricity. Currently, wave power generation is not a commercially utilized technology as the first experimental wave farm opened in Portugal in 2008 with potential plans for further experimental wave farms.

1.2.9 Wind Power

With the exception of hydroelectric power, wind power is the most utilized renewable energy source. As an alternative energy, wind power is widely distributed, clean and plentiful and uses little land. Currently, wind energy comprises 2.5% of the total worldwide electricity usage. Additionally, wind power generation is growing around 25% annually. It is exceptionally attractive from a capita standpoint as the cost per unit of energy produced is very similar to that of new coal and natural gas installations. Similar to other alternative energies, wind power has its detractors, but while those technologies tend to have detractors of the environmental variety, detractors of wind power are typically concerned with site aesthetics. In recent years a new form of wind power has gained attention for the amount of electricity it may be able to produce. This new technology termed high-altitude wind power (HAWP) captures the power of winds high in the sky through a tether and cable. The amount of energy that may be produced from HAWP is under debate however, as values ranging from 7.5 TW to 1700TW have been calculated.

1.2.10 Nuclear

While nuclear energy is not technically renewable, it still falls under the category of alternative energy, as it is not related to fossil fuels. Currently, nuclear power plants provide approximately 14% of the global electricity. However, nuclear power is predominately used by developed nations, with France, Japan and the United States accounting for 50% of the electricity generated via nuclear reactors. In the wake of the Fukushima Daiichi nuclear disaster, there has been a push for many countries to phase out their nuclear programs. As such, the IEA has halved the estimate of added nuclear generation by the 2035. Other nuclear power accidents, such as the Chernobyl disaster and the Three Mile Island incident
have done little to help assuage the public fear of nuclear energy production.\textsuperscript{53} Despite these incidences, nuclear power is still the safest form of energy generation in the history of mankind.\textsuperscript{54-56} Additionally, research continues into making nuclear energy even safer, predominately in the design of reactors.\textsuperscript{57} Furthermore, the cost of building and maintaining nuclear power plants has become cost prohibitive and many utility companies are choosing not to build plants or are even closing existing plants for these reasons. Nevertheless, nuclear power still has many proponents, such as the World Nuclear Association and the International Atomic Energy Agency (IAEA). Both of which maintain that nuclear power is a viable and sustainable energy source which can be utilized to help reduce carbon emissions.\textsuperscript{58} Despite public fear, some countries are ramping up nuclear power plant construction, primarily China, which is currently building around 25 nuclear power plants and has plans to build many more.\textsuperscript{59}

1.3 Energy Conclusion

Overall, there is a range of alternative, renewable energy sources that are capable of relieving humanities dependence on fossil fuels. While many of these alternatives are currently employed to some degree, their usage must be increased. To do so, research is necessary to reduce their cost and to increase their efficiency. There will come a time when fossil fuels will not be a feasible energy source. It is therefore imperative to optimize the alternative, renewable energy sources that are known to us now, such as biofuels and solar energies, while continuing to explore new ideas such as HAWP.
Table 1-1: Energy Sources

<table>
<thead>
<tr>
<th>Renewable Energies</th>
<th>Non-Renewable Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biofuel</td>
<td>Fossil:</td>
</tr>
<tr>
<td>Biomass</td>
<td>Coal</td>
</tr>
<tr>
<td>Geothermal</td>
<td>Petroleum</td>
</tr>
<tr>
<td>Hydroelectricity</td>
<td>Natural Gas</td>
</tr>
<tr>
<td>Solar Photovoltaic</td>
<td>Radioactive Fuel:</td>
</tr>
<tr>
<td>Solar Thermal</td>
<td>Fission</td>
</tr>
<tr>
<td>Tidal Power</td>
<td>Cold Fission</td>
</tr>
<tr>
<td>Wave Power</td>
<td>Fusion</td>
</tr>
<tr>
<td>Wind Power</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 2: Photovoltaic Basics

Photovoltaics convert sunlight into useable electric energy. The fundamental physics of photovoltaics is well understood with the following references being excellent sources of information. The following will be the basics of photovoltaics, as the understanding of any technology starts with the basics.

2.1 Solar Irradiance

Photovoltaic energy generation is possible due to the sun’s radiation. A photon of light has a specific energy, $E_{ph}$, and wavelength, $\lambda$, related to each other through:

$$E_{ph} = \frac{hc}{\lambda} \quad [2.1]$$

where $h$ is Planck’s constant and $c$ is the speed of light in a vacuum. Thus, photons can be characterized by either their energy or wavelength.

The solar constant is a measure of the flux density of electromagnetic radiation that reaches earth. The solar constant is, however, a misnomer as the electromagnetic radiation flux density changes with solar activity and changes in distance from the sun as the earth orbits. The solar constant has been measured by satellites to be 1361 W/m$^2$. In 2000 the American Society for Testing and Materials (ASTM) developed an Air Mass Zero (AM0) reference spectrum for testing of photovoltaics for space applications. The Earth’s atmosphere interacts greatly with the solar radiation, attenuating the solar spectrum over its whole range. As such, additional Air Mass units are used to account for this. AM1 represents the intensity at solar noon at the equator while AM2 is utilized for high latitudes. However, a common standard for testing of terrestrial photovoltaics has been adopted by industry. This is the AM1.5 spectrum at 1000 W/m$^2$. These are the conditions set by the National Renewable Energy Laboratory (NREL) and correspond to a clear day with sunlight incident upon a sun facing 37 degree tilted surface with a sun angle of 41.81 degrees above the horizon. These conditions are that which are found in the United States at the solar noon near the spring and autumn equinoxes. The AM0 and AM1.5 ground spectrums are presented in Fig. 2-1. Interactions between atmospheric chemicals/compounds and photons account for the additional dips in the terrestrial AM1.5 spectrum.
2.2 Photovoltaic Materials Properties

The materials properties are of great interest as they can greatly affect the electrical properties of photovoltaics. The basic materials properties pertaining to photovoltaics will be covered in this section. For a more in-depth look as semiconductor materials properties please refer to the following sources.12-15

2.2.1 Crystal Structure

While there are some amorphous and polycrystalline solar cells, the best performance is obtained from single crystal photovoltaics. A crystal structure is that which is composed of a set of atoms arranged in a periodic manner which exhibit order and symmetry over a long range. The structure of a crystal is important as many of its physical properties, such as electrical and optical characteristics, are influenced by the crystal form. Background on crystallography can be found in the literature.16-18

2.2.2 Energy Band Formation

Every object has a wave function, which contains all observable properties of that object. However, the wave function itself cannot be observed. With respect to electrons, when atoms are separated from one another, such that there are no interactions between the two, electrons for the two atoms are allowed to occupy the same quantum states. However, once the atoms begin interacting with one another the electrons are no longer allowed to have the same quantum states. This applies strictly to fermions and has been termed the Pauli exclusion principle after the Austrian physicist who formulated the principle, Wolfgang Pauli.19 As dictated by the Pauli exclusion principle, when atoms are brought together to form a solid there is a splitting of the discrete energy levels within the atoms. In solids where many atoms are in close proximity to one another continuous bands form as presented in Fig. 2-2.20 The highest occupied molecular band is termed the valence band, while the lowest unoccupied molecular band is termed the conduction band. The separation between these two bands is the bandgap of the material.

The relationship between the valence band and the conduction band determines the electrical characteristics of the material. Conductors have conduction bands which overlap
with valence bands; essentially, giving the lattice of these materials a sea of electrons which can move and are not locked to atoms. Insulators have a very large separation between valence and conduction bands, while semiconductors have an intermediate separation between the two bands. A more detailed and rigorous investigation to the solution of the actual band structure involves solving the Schrödinger equation, typically through the utilization of the Bloch theorem. This is beyond the scope of a basic understanding of solar cell physics and will not be discussed.

2.2.3 Electrons and Holes

For an intrinsic semiconductor at absolute zero, all electrons are bound to atoms in the crystal lattice and are in the valence band. As the crystal lattice begins to heat, lattice vibration imparts kinetic energy to the electrons, allowing some of them to be promoted into the conduction band. These promoted electrons are now capable of electrical conduction. When these electrons are promoted they leave behind voids in the valence band. These voids can be treated as positively charged particles that are also capable of electoral conduction and have been termed holes. This thermal excitation from absolute zero is presented graphically in Fig. 2-3. Holes are utilized in the valence band because they are easier to keep track of as opposed to the large number of electrons. Thus, intrinsic semiconductors have equal numbers of electrons and holes at all times.

Carrier concentration can be increased by using impurity atoms, termed dopants. These dopants have different valence shell configurations than the host lattice elements. Dopants with a larger number of valence electrons will form energy levels just below the conduction band. These dopants are termed donors and create n-type semiconductors. Dopants with a smaller number of valence electrons will form energy levels just above the valence band. These dopants are termed acceptors and create p-type semiconductors. Thus, doped semiconductors, as opposed to intrinsic semiconductors, do not have the same number of holes and electrons. Doping has been graphically represented in Fig. 2-4.

While there is some thermal excitation of carriers taking place in photovoltaics, the vast majority of carriers are created through the absorption of photons. When any semiconductor is exposed to light, photons with energy greater than the material bandgap
will be absorbed by electrons in the valence band. These electrons will be promoted into the conduction band and result in a hole being created in the valence band. Photons with energy less than the material bandgap will pass through the material. Carrier generation via photon absorption is presented graphically in Fig. 2-5.

2.2.4 The Formation of Junctions

To understand the formation of junctions we must first define a new parameter, the Fermi level. A Fermi level is a hypothetical energy level that has 50% probability of being occupied at thermodynamic equilibrium. Carrier collection is accomplished through the creation of p-n junctions. When materials of two different doping types are brought together, their Fermi levels line up such that they are continuous across the junction, as presented in Fig. 2-6. The end result is the creation of a depletion region and electric field across the junction.

With respect to photovoltaics, carriers generated via photon absorption are separated by the electric field, with holes and electrons being swept in opposite directions. This separation of charge results in a photovoltage, $V_{OC}$, being produced at open circuit conditions and a photocurrent, $I_{SC}$, produced at short circuit conditions.

2.3 Device Parameters and Principles

The ultimate goal of a photovoltaic cell is to generate electricity and power. In order to accomplish this, the solar cell must produce both a photocurrent and a photovoltage. In this section, device parameters like photocurrent, photovoltage, fill factor and efficiency will be discussed in general.

2.3.1 Photocurrent

The photocurrent produced by a photovoltaic cell is directly related to the number of photons that are absorbed. Thus, materials with a low bandgap are capable of producing greater photocurrents as more electrons are promoted from the valence band into the conduction band. This assumption only works, however, if one assumes all absorption occurs at the surface of materials. In actuality, this is not the case and absorption occurs constantly,
assuming it can occur, throughout a material until the photons are depleted. Thus, generating current is also dependent on the optical absorptive properties of materials. For example, gallium arsenide (GaAs) has a much higher absorption coefficient than germanium (Ge). As such, thicker layers of Ge are required to absorb photons.

With respect to photocurrent, there are two parameters that have been defined for solar cells, each playing an important part in ultimately determining the efficiency of any cell. The first of these parameters is the short-circuit current ($I_{SC}$). The $I_{SC}$ is a measure of the current produced by the cell when the cell is shorted (zero resistance). The second of these parameters is the maximum-power current ($I_{MP}$). The $I_{MP}$ is more representative of operational performance of a solar cell as it is the current produced under maximum power conditions. Maximum power conditions will be discussed in more detail in the Fill Factor section.

2.3.2 Photovoltage

The voltage of a photovoltaic single junction cell is directly related to the bandgap of the material used. Higher bandgap materials have promoted electrons with greater energy than lower bandgap materials. Thus, as these higher potential energy electrons build up on the terminals of the p-n photovoltaic device they impart a larger potential energy across the device.

As with photocurrent, there are two parameters that have been defined for solar cell photovoltage. Again, each of these parameters plays an important part in ultimately determining the efficiency of any cell. The first of these parameters is the open-circuit voltage ($V_{OC}$). The $V_{OC}$ is a measure of the photovoltaic output voltage when no current is flowing from the device. The second of these parameters is the maximum-power voltage ($V_{MP}$). As with $I_{MP}$, $V_{MP}$ is more representative of the solar cell operational performance as it is the voltage output produced under maximum power conditions. Maximum power conditions will be discussed in more detail in the Fill Factor section.
2.3.3 Fill Factor

Fill factor (FF) is used to describe the degree to which the maximum power conditions of any operating photovoltaic device match the upper limits determined by $I_{SC}$ and $V_{OC}$. The equation for FF is:

$$FF = \frac{I_{MP}V_{MP}}{I_{SC}V_{OC}} = \frac{Power_{Max}}{I_{SC}V_{OC}}. \quad [2.2]$$

FF for the most efficient photovoltaic cells is around 85% at one sun.

2.3.4 Efficiency

Solar cell efficiency is the ratio of maximum power generated by a solar cell to the incident energy from the sun as presented in the following equation:

$$\eta = \frac{Power_{Max}}{Incident Solar Energy}. \quad [2.3]$$

Terrestrial solar cells are measured under standard testing conditions of 25°C and an irradiance of 1000W/m² with an AM1.5 spectrum.
Figure 2-1: AM0 and AM1.5 solar spectrums.
Figure 2-2: Energy band formation as Si atoms are brought together to form Si bulk solid. 2.35 Å is the equilibrium distance for interatomic spacing in Si.

Figure 2-3: Thermal excitation of carriers. The circles represent electrons which can be promoted thermally from the valence band into the conduction band.
Figure 2-4: Doping of materials to make carrier generation easier. The circles represent electrons which can either be excited from the valence band into an acceptor level or from a donor level into the conduction band.

Figure 2-5: Carrier excitation through the absorption of a photon. The circles represent electrons which can be promoted due to the absorption of a photon with energy greater than that of the materials bandgap.
Figure 2-6: (A) A p-type and n-type material separated with their respective $E_f$ labeled and (B) the resultant p-n junction created by bringing the materials together.
CHAPTER 3: Multi-junction Photovoltaics

Due to their inefficient utilization of the solar spectrum, single junction photovoltaics are limited in their potential efficiencies. One obvious solution to this limitation is to use a series of junctions to absorb different regions of the solar spectrum. Photovoltaic cells utilizing this technology are termed multi-junction solar cells (MJSC). What follows is a general overview of MJSC technology, the considerations that must be made and ways of improving the technology.

3.1 Multi-junction Solar Cell Design

MJSCs efficiently utilize a larger range of photons by using a combination of semiconductor materials with different bandgaps. The prototypical MJSC is the Ge/(In)GaAs/InGaP triple junction (3J), the spectrum breakdown of which is presented in Fig. 3-1. For comparative purposes, the bandedge for the typical Si solar cell is also included in Fig. 3-1. Due to better utilization of the solar spectrum, MJSC do not suffer from heat losses as typical single junction solar cells do. A diagram showing the lattice constant and bandgap for various semiconductor materials is presented in Fig. 3-2.¹

3.2 Materials Selection

Building MJSCs is a complicated endeavor that necessitates compromise in selecting materials. There are three main parameters that must be considered. These parameters are lattice constant, bandgap and current matching.

3.2.1 Materials Selection Based on Lattice Matching

It is of the utmost importance that the materials selected for MJSC applications have compatible lattice structures. A list of semiconductor materials used in MJSCs is presented in Table 3-1 along with the lattice constant and crystal lattice type for each material. As can be seen, many of the materials utilized in MJSC have either a diamond or zinc-blend crystal structure. These two crystal structures are the same in that they are each two interpenetrating face centered cubic (FCC) sub-lattices shifted by ¼ along the [111]. When all the atoms the same within the structure, as is the case for Si and Ge, the structure is called diamond.
However, for binary materials, each of the sub-lattices is comprised of different elements and is termed Zinc-blend. The bonding between elements is still tetrahedral, as in the diamond structure, but the bonds are all shared between the two elements that comprise the binary semiconductor.

In addition to lattice structure compatibility, the lattice constant of the materials is also important. The lattice constant is a measure of the distance between two atoms occupying lattice points on the corners of the unit cell. It is highly desirable to match the lattice constant of the various layers, although not all MJSC architectures follow this. If there is a mismatch between lattice constants among the materials, defects and dislocations will result as the materials relax. The thickness at which this relaxation occurs is termed the critical layer thickness and can be predicted. Defects and dislocations act as recombination centers which result in $V_{OC}$, $I_{SC}$ and FF degradation.

3.2.2 Materials Selection Based on Bandgap

As the photons comprising the solar spectrum have many different energies, it would be possible, in theory, to select a different material to match each region of the solar spectrum. Additionally, the optimum stack of junctions would depend on where the MJSC was to be operated as the spectrum changes depending on location. A theoretical “infinite junction” would have an efficiency of $\sim 87\%$. However, due to lattice matching conditions that must be met; it is not feasible to build MJSC in this manner. The idea of dividing the solar spectrum among materials is still utilized, but only as far as lattice matching conditions allow. The general architecture for a MJSC is presented in Fig. 3-3. The subcells within this MJSC are stacked such that the material bandgaps of the semiconductors decrease as you move into the MJSC. The highest energy photons are absorbed in the top subcell, allowing lower energy photons to pass through unaffected.

Elements from column III and column V of the periodic table result in semiconductor alloys that are easily built into MJSC. This is because a range of bandgaps can be obtained by utilizing different V/III alloys. It should be noted that the degree to which the bandgaps can be selected is also dependent, to a degree, on the lattice constant of the individual materials. A list of the typical materials utilized in MJSC applications is presented in Table 3-1.
3.2.3 Materials Selection Based on Current Matching

Due to the subcells within a MJSC being connected in series, the current generated by the MJSC will be limited to that of the smallest subcell current. This is explained in greater detail in Fig. 3-4. As such, it is desirable that the subcells produce equal current. Unfortunately, current MJSC suffer greatly from inadequate current matching among subcells. Work, including this research, is underway to improve current matching in these structures.

3.3 Multi-junction Solar Cell Efficiency Increase

MJSC efficiency can be improved primarily through two ways. First, MJSC efficiency can be increased through the improvement of current matching among the subcells. Second, MJSC efficiency can be improved by utilizing high solar concentration.

3.3.1 Improving MJSC Efficiency through Bandgap Engineering and Better Current Matching

One way in which MJSC efficiency can be improved is through better current matching among the subcells and through the development of a material with a bandgap of approximately 1.0eV. This has been attempted through a number of different approaches including metamorphic (MM)\textsuperscript{5-9} growth, inverted metamorphic (IMM)\textsuperscript{10-14} growth, dilute nitride materials\textsuperscript{15-19} and pseudomorphic multi-quantum wells (MQWs) structures.\textsuperscript{19-31}

3.3.1.1 Efficiency Improvements: Metamorphic Structure

One solution to the issue of current matching in MJ solar cells is MM growth. In this method, a graded InGaAs buffer layer is grown metamorphically on top of the Ge bottom subcell. This acts to change the lattice parameter of subsequent growth, and allows for lower bandgap materials for both the middle and top subcell through the use of higher indium compositions for each. However, metamorphic growth does present challenges. As the InGaAs buffer layer is grown, it relaxes. This relaxation introduces defects and dislocations that propagate along the growth direction, which negatively impacts the performance of the top cell as it is highly susceptible to dislocations. This is especially deleterious due to the fact
that the majority of the power produced by the cell comes from the top and middle sub cells. It is for this reason that present metamorphic MJ cells do not reach the efficiencies that would be expected by current matching models.\textsuperscript{5-9}

### 3.3.1.2 Efficiency Improvements: Inverted Metamorphic Structure

Another solution to overcoming the current matching issues in MJSCs is IMM growth. Similar to MM growth, a graded InGaAs buffer layer is utilized to change the lattice constant of subsequent growth. However, in this method the solar cell is grown upside down with the top cell grown lattice matched to the substrate.\textsuperscript{10-14} This maintains the top cell as defect free, and also limits the defects from the buffer region into the lower cells which are not as easily affected by defects as the top subcell is. Additionally, the substrate is removed which lowers the total weight of inverted metamorphic MJ cells, great for space applications where payload weight is the main cost consideration. However, the removal of the substrate adds additional complexity to the processing and fabrication of the cell, which consequently results in yield losses and increases the cost of the final product.

### 3.3.1.3 Efficiency Improvements: Dilute Nitride Based Solar Cells

An additional material which may increase current matching in present MJ cells is InGaAsNSb. While this material system originally suffered greatly from poor minority carrier lifetime and diffusion length, it has been improved greatly in recent years.\textsuperscript{15-19} However, there still remain some major obstacles to this material becoming a viable option for MJSCs. In particular, the growth is accomplished via molecular beam epitaxy (MBE). MBE is a growth system that is not suited well for large scale industrial applications like metal organic chemical vapor deposition (MOCVD). This is a major hindrance to InGaAsNSb as the bulk of commercial MJSCs are produced via MOCVD.

### 3.3.1.4 Efficiency Improvements: Pseudomorphic GaAs i-layer MQW Structure

While both metamorphic and inverted metamorphic growth each suffer to a varying degree from the defects introduced via the InGaAs buffer, it is alternatively possible to improve current matching via pseudomorphic growth. This adds a stress balanced MQW
structure to the intrinsic layer, i-layer, of the middle GaAs subcell. The research herein
details the development and implementation of such a structure.

3.3.2 Efficiency Improvements: Solar Concentration

For III-V MJSC’s, concentrators are of great importance for terrestrial applications.
By concentrating the solar radiation, the total power produced per area of active solar cell is
increased, helping to justify the typically high costs of III-V solar cells. Additionally,
concentration improves the performance and efficiency of MJSCs due to increased $V_{OC}$.
However, the ability for a cell to work under concentration is at present hindered by the
instability of the tunnel junction (TJ) utilized to connect the subcells within the MJSC in
addition to the sheet resistance and heat generated. TJs will be discussed in more detail in
chapter 8. By improving the TJs within MJSC, higher concentrations could be used, further
improving the efficiency of III-V MJSC technology.

Table 3-1: Selected Semiconductor Parameters

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Bandgap (eV)</th>
<th>Lattice Type</th>
<th>Lattice Constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.11$^{32}$</td>
<td>Diamond</td>
<td>5.43$^{32}$</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.43$^{32}$</td>
<td>Zinc-Blend</td>
<td>5.65$^{32}$</td>
</tr>
<tr>
<td>InAs</td>
<td>0.36$^{32}$</td>
<td>Zinc-Blend</td>
<td>6.06$^{32}$</td>
</tr>
<tr>
<td>GaP</td>
<td>2.26$^{32}$</td>
<td>Zinc-Blend</td>
<td>5.45$^{32}$</td>
</tr>
<tr>
<td>AlAs</td>
<td>2.16$^{32}$</td>
<td>Zinc-Blend</td>
<td>5.66$^{32}$</td>
</tr>
<tr>
<td>Ge</td>
<td>0.67$^{32}$</td>
<td>Diamond</td>
<td>5.65$^{32}$</td>
</tr>
<tr>
<td>InGaP (Ge matched)</td>
<td>1.8-1.9$^{13}$</td>
<td>Zinc-Blend</td>
<td>5.65</td>
</tr>
</tbody>
</table>
Figure 3-1: Solar spectrum breakdown for the industry standard Ge/(In)GaAs/InGaP MJSC. Higher efficiency is accomplished through better utilization of the spectral regions as compared to Si, which is represented by the line.
Figure 3-2: Bandgap energy and lattice constant of various III-V semiconductors at room temperature.
Figure 3-3: General architecture for multijunction solar cells.

\[ E_{g1} > E_{g2} > E_{g3} \]
Figure 3-4: A visual diagram to explain the current limiting problem due to the GaAs middle subcell in a typical 3J MJSC consisting of InGaP/GaAs/Ge.
CHAPTER 4: MOCVD Growth

4.1 MOCVD Growth

Metal-organic chemical vapor deposition (MOCVD) is a growth method in which a thin solid film, usually a semiconductor, is deposited on a solid substrate using organometallic compounds as sources. MOCVD is often used interchangeably with metal-organic vapor phase epitaxy (MOVPE) and organo-metallic vapor phase epitaxy (OMVPE). Throughout this dissertation MOCVD will be used exclusively. The electronic and optoelectronic devices produced via MOCVD are used in a myriad of applications including hetero-junction binary transistors (HBTs) for cell phones\textsuperscript{1-2}, LEDs in traffic lights\textsuperscript{3-4} and solar cells for electrical generation\textsuperscript{5}. Common to every epitaxial growth technique, MOCVD has its strengths and weaknesses. Among its strengths, MOCVD is the most flexible growth technique capable of large scale production. The reactors are relatively simple when compared to other growth methods and high purity growth is easily obtained with reasonable interface quality. However, the sources employed in MOCVD are oftentimes expensive and many are hazardous. Additionally, MOCVD has the most parameters to control for proper thin film deposition. As such, various factors can interfere with the epitaxy process. Additionally, the thermodynamic and kinetic processes of MOCVD are still not yet fully understood. Stringfellow’s text is a great source and offers details on a wide array of topics relevant to MOCVD epitaxy.\textsuperscript{6} A list of pros and cons for other thin film growth techniques, in addition to MOCVD, is presented in Table 4-1.

4.2 Metalorganic Precursors

In MOCVD, there are several species utilized to complete the growth of any epitaxial film. These include vapor sources which are premixed with either nitrogen or hydrogen and metal-organic precursors. Both of which will be discussed in some detail in this section.

4.2.1 Metalorganic Precursors: Vapor Sources

Gaseous sources are high purity sources premixed by specialized companies. They are packaged in high pressure tanks and the outlet pressure is regulated for injection into
dilution manifolds. The dilution manifolds allow for a wider range of source fluxes which can be utilized during MOCVD growth.

4.2.2 Metalorganic Precursors: Bubblers

Organometallic precursors are packaged in stainless steel bubblers, a general schematic of which is presented in Fig. 4-1. The bubbler inlet tube extends nearly to the bottom of the source liquid. As the carrier gas is delivered, it is saturated as it moves though the liquid organometallic precursor. The saturated vapor then moves out through the bubbler exit and is either routed to the vent or run lines via the run/vent manifold. The Thomas Swan MOVCD system can accommodate up to seven bubblers and has been modified to handle an 8th.

There are several desirable properties of precursors that should be taken into account when selecting them. Ideally, although not always possible, they should have a low toxicity. Additionally, it is best if the precursors are liquid at the temperature they are to be used. Liquid sources result in more reproducible growth in addition to good long term stability. Metal-organic precursors should have a suitable vapor pressure for the application in which they are being used. Additionally, their pyrolysis temperature should be similar to the growth temperature to ensure proper decomposition of the precursors. Finally, it is best if the precursors result in low carbon contamination in the epitaxial films. This carbon contamination is typically due to the formation of CH₃ radicals that are a byproduct of the pyrolysis reaction. A list of the metal-organic precursors utilized in this research is presented in Table 4-2 along with pros and cons. Additionally, vapor pressure charts and equations for the precursors utilized in this research are presented in Fig. 4-2, 4-3 and 4-4 for column III, column V and dopant sources, respectively.

4.3 Basic Components of MOCVD

All MOCVDs have four basic components: a run/vent manifold, a reactor with a heated susceptor, a vacuum/exhaust system and a scrubbing unit. Each of these component systems will be discussed independently in the following sections, in the context of the research explored in this dissertation.
4.3.1 Basic Components of MOCVD: Run/Vent Manifold

Precursor delivery is regulated by a computer controlled system utilizing a commercially available software package developed by Thomas Swan (now Aixtron). In general, structures grown via MOCVD are composed of multiple materials and the interfaces between these layers should be sharp to obtain optimum performance of the structure. For this reason, a run/vent manifold, schematic presented in Fig. 4-5, is used to help maintain a smooth crystal surface when switching precursor sources. The manifold works by having a carrier gas flow through both lines at all times. The run line goes to the reaction chamber while the vent line bypasses the reactor and goes to the exhaust manifold. The precursor is directed into either the run line or vent line by a block of valves. When a new source is required for the epitaxial growth, the source is first turned on to the vent line. This helps to prevent the growth from being affected by pressure changes due to source turn on. Additionally, both the vent and run lines are held at the growth pressure, further ensuring there are no pressure surges in the MOCVD system as growth is occurring. When the source is needed for growth, it is switched from the vent line into the run line. To accommodate the instantaneous pressure change that would occur during this switching, the MOCVD is equipped with makeup lines to keep the pressure in both the vent and, more importantly, the run line from changing. This is especially important when growing the multi-quantum well structure as trimethyl indium (TMIn) and tributyl phosphine (TBP) vent/run switching occurs frequently. The block for run/vent switching is designed for rapid switching with very small dead volume. The MOCVD is equipped with two run/vent manifolds as the column III and column V compounds have to be separated to prevent gas phase reactions.

4.3.2 Basic Components of MOCVD: Susceptor and Reactor Chamber

The substrates are loaded into the reaction chamber and placed onto the susceptor. In general, a susceptor is a material which will absorb electromagnetic energy and convert it into heat. The susceptors used for this research are graphite coated with silicon carbide (SiC). The SiC coating is needed to contain the carbon and prevent contamination from the susceptor. The temperature of the susceptor is maintained by a 7500 W Ameritherm radio frequency (RF) power source. Susceptor rotation is very important for growth uniformity.
Through rotation, all areas of the substrate are equally exposed to both III and V column sources, resulting in better uniformity. Additionally, rotation of the susceptor helps to maintain a uniform growth temperature throughout the substrate. New susceptors undergo a bake to prepare them for MOCVD growth. The procedure is as follows:

1. The MOCVD reactor chamber is purged via a 10 cycle pump purge sequence.
2. The susceptor is slowly ramped to a temperature of 350°C over the course of 2400 secs to drive out any water vapor from the graphite and SiC coating.
3. The susceptor is slowly ramped from 350°C to 900°C over the course of 2400 secs to drive deeper water vapor from the susceptor and help relieve any residual stresses from the fabrication process gradually.
4. The susceptor is kept at 900°C for 1200 secs.
5. The susceptor is cooled to 600°C in preparation for a GaAs epitaxial coating.
6. GaAs is deposited on the susceptor for 900 sec utilizing 3.9 µmol/min of TMGa and 76.5 µmol/min of TBAs.
7. At the conclusion of GaAs deposition the susceptor is cooled to 450°C under an overpressure of TBAs to prevent arsenic desorption.
8. The new susceptor bake is concluded with a 10 cycle pump purge sequence.

The reactor utilized in this research is a custom quartz design, a picture of which is presented in Fig. 4-6. The reactor chamber was produced by Prism Research Glass (Raleigh, NC). Because this is a hand built reactor and the growth rate of the thin films is solely dependent on the delivery of the column III species, reactor orientation must always be kept constant for reproducible results.

Initially for the research presented herein, multiple reaction chambers were fabricated with the intention of using all for growth. However, it became apparent that chambers had different fluid dynamics. As such, no two chambers grew the same. This non-uniformity in growth from one chamber to the next has been attributed to the fact that each is handmade, making exact replication impossible. This phenomenon is unique only to research, in comparison to large scale production which typically utilizes different reactor arrangements that are not handmade.
4.3.3 Basic Components of MOCVD: Vacuum/Exhaust System

The pressure in the Thomas Swan reactor is controlled by a 25 cubic foot per minute (CFM) Alcatel rotary vane pump and a micro-stepping butterfly valve, both of which are located downstream in the exhaust. The pressure is maintained by a feedback loop made up of a Baratron pressure sensor near the reactor exit and a standard pressure controller. To reduce the occurrence of gas phase reactions, the MOCVD growth is accomplished at a pressure of 200 torr. Reducing the pressure increases the mean free path of the molecules in the reaction chamber, resulting in fewer collisions. This in turn results in fewer gas phase reactions taking place and a better epitaxial growth surface morphology.

In addition to regulating the reactor pressure, the vacuum/exhaust system carries reaction byproducts away from the reactor and to the scrubber. After the reaction chamber, many of the byproducts are volatile and toxic. To help further break these byproducts down, they are passed through a pyrolysis furnace (pyrofurnace) that operates at 400°C. The pyrofurnace is a heated section of tubing containing stainless steel beads to provide a larger surface area over which decomposition can take place. The exhaust is then passed through a particle filter. At this point many of the remaining gaseous byproducts are safe and can be released into the surrounding environment. However, any arsenic containing byproducts must be removed from the exhaust via the scrubber.

4.3.4 Basic Components of MOCVD: Scrubber

The scrubber, produced by Novapure (Norwalk, CT), removes any toxic byproducts from the exhaust that have not already reacted to form inert products. The exhaust gas passes through a proprietary chemisorptive resin before returning to a common exhaust line. This chemisorptive resin reacts with the remaining reactive species in the exhaust and sequesters them. The trapped species are then oxidized periodically to render them inert. The oxidation procedure is as follows:

1. Open the compressed air tank connected to the Novapure scrubber.
2. Set the nitrogen purge on and use the two Matheson flow meters within the scrubber cabinet to set the flow.
3. Allow the oxidation to take place for a time required to react all phosphorus and arsenic species that may be present in the scrubber. This time is calculated using the total flow of
phosphorus and arsenic since the last oxidation procedure. Two hours will generally suffice if no calculation is performed.

4. Watch to make sure there are no large temperature changes within the scrubber. There are 5 thermocouples connected to an Omega DP80 readout. Each should be checked.

5. Once the oxidation procedure has finished switch the scrubber purge back to off and close the compressed air.

4.4 Substrates, Substrate Preparation and Substrate Loading

Selection of the proper substrate is imperative for proper MOCVD growth. Additionally, due to the setup of the utilized MOCVD reactor, cleavage of the substrates was necessary. Proper sample preparation procedures prior to substrate loading must be followed to ensure the cleavage of the substrates does not detrimentally effect the epitaxial growth.

4.4.1 Substrates

MOCVD growth requires the use of a substrate, onto which all subsequent epitaxial growth occurs. Substrate wafers can be purchased in a variety of orientations, for a variety of materials. These materials and orientations may be selected to produce varying results. For this research, all films were grown on (001) GaAs substrates oriented with a 2° off-cut toward the [011] direction from Wafer Technology Ltd (United Kingdom). Wafer Technology Ltd. produces these wafers using a vertical gradient freeze method which produces the lowest dislocation density of all production techniques. The wafers are mis-oriented, also termed off-cut and vicinal, to produces steps which encourage proper growth of the thin film. This is because the diffusion of the atoms on the surface is affected by the atomic steps on the substrate, termed step flow. Atoms preferentially incorporate at step edges. Wide steps allow for long diffusion lengths with fewer step edges while narrow steps reduce the diffusion coefficient. For the most part, step width is dependent on substrate off-cut with lower off-cuts resulting in larger step widths. Thus by utilizing a vicinal substrate, as opposed to an on-axis substrate, better film qualities can be obtained since the atoms incorporate easily at step edges and three-dimensional nucleation and growth is suppressed. A diagram of precursor diffusion for an on-axis and off-cut substrate is presented in Fig. 4-7.
4.4.2 Substrate Preparation

Many MOCVD reactors utilize wafers larger than 3”. However, to cut down on cost, the research presented herein utilized wafers that were cleaved into 14 mm × 14 mm squares. A 2” wafer results in 7 usable 14 mm × 14 mm substrates. Extreme care was taken when handling the substrates, as any surface damage would have severely affected the quality of the epitaxial growth. As such, all substrate manipulation was handled with Teflon coated tweezers. Additionally, before loading any substrate into the reaction chamber, it was first cleaned in a Teflon beaker by the following procedure:

1. Rinse the substrate well with isopropyl alcohol while ensuring the substrate is never exposed to air. The isopropyl alcohol removes any residual particles from the cleaving process. Isopropyl alcohol is used for this process due to the fact that it is a high purity solvent with a surface tension sufficient enough to remove the particles.
2. Rinse the isopropyl alcohol out with hexane while ensuring the substrate is never exposed to air. The hexane removes any oily/hydrophobic materials that may have contaminated the wafer during the cleaving process. The substrate, completely covered with hexane, should be placed in the sonic bath for no less than 2 mins to ensure the best cleaning.
3. Rinse the hexane out with acetone while ensuring the substrate is never exposed to air. While acetone will help to remove any remaining oily/hydrophobic materials remaining on the substrate, it is predominately used as a step between the hexane and methanol rinses as hexane and methanol are completely immiscible in one another. This is not the case for acetone and methanol. This step does not require any ultrasonic action.
4. Rinse the acetone out with methanol while ensuring the substrate is never exposed to air. The methanol acts to dissolve any hydrophilic compounds that may have contaminated the substrate during the cleaving process. The substrate, completely covered with methanol, should be placed in the sonic bath for no less than 2 mins to ensure the best cleaning.
5. Rinse the methanol out of the beaker using reverse osmosis/de-ionized (RO/DI) water for several minutes. This is no less than a 10 time (10×) rinse process. It is imperative that the substrate is never exposed to air during this process.

At this point the substrate is properly cleaned of any particles, hydrophobic materials and hydrophilic materials that were introduced during the cleaving process. However, a chemical process is now needed to properly prepare the substrate for epitaxial growth. This process, which is always done immediately following solvent cleaning, is as follows:

1. With little water remaining from the last step of the solvent rinse, but enough to ensure the sample is not exposed to air, add sulfuric acid (H₂SO₄). The H₂SO₄ removes any residual ions,
both metal and non-metal, from the surface of the substrate which were introduced during the polishing process of the wafer. H$_2$SO$_4$ will also work to remove any oxide on the sample prior to etching.

2. Rinse thoroughly with RO/DI water for several minutes while ensuring the substrate is never exposed to air. This is a 10× rinse process.

3. Etch the substrate for 30sec with a solution of the following:
   a) 20ml of DI/RO water.
   b) 4ml of ammonium hydroxide (NH$_4$OH).
   c) 4ml of hydrogen peroxide (H$_2$O$_2$).

4. With this etch the H$_2$O$_2$ is added last to the solution, as this compound degrades when exposed to light and heat. This etch solution is utilized to remove any surface and subsurface damage on the substrate and yields a very good surface for epitaxial growth. The etching should only be allowed to proceed for 30 sec to ensure a proper surface is obtained without the danger of over etching. Following this etch procedure should result in ~1 µm of substrate material being etched.

5. Rinse thoroughly with RO/DI water for several minutes while ensuring the substrate is never exposed to air. This is a 10× rinse process.

6. Rinse in hydrochloric acid (HCl) to remove any native oxides that were built up from the previous rinse/etch steps. It is imperative that this HCl etch only be allowed to occur for 1 min. It has been found that etching in HCl for longer than 1 min will result in a sample that is hydrophobic.

7. Rinse thoroughly with RO/DI water for several minutes while ensuring the substrate is never exposed to air. This is a 10× rinse process.

8. Remove the substrate from the beaker with as much water on its surface as possible. Place the substrate on the vacuum chuck and blow off the water quickly using pure, dry nitrogen. The blow off procedure should be done by directing a jet of nitrogen from one edge of the now cleaned substrate to the opposite edge, driving the water off in a sheet like action.

9. Load the now cleaned substrate into the reactor.

It is imperative that the substrate never be exposed to air during the solvent/etch procedure until the conclusion of the blow off step. Exposing the substrate to air will result in the formation of hazy spots which may not be noticed until after epitaxial growth. Additionally, if a hydrophobic sample is encountered after the cleaning procedure, discard the substrate and start the solvent/etch procedure over with a new substrate. A hydrophobic sample will result in a hazy epitaxial growth.
4.4.3 Substrate Loading

The reactor is the location of epitaxial growth. It is maintained at precise temperatures and pressures, and is supplied with the metal-organic vapors. Substrates are loaded into the reactor by removing the quartz reaction chamber. The substrate is then placed onto the susceptor. A cleaned quartz chamber is then placed over the substrate and susceptor. During growth, the quartz chamber accumulates a significant amount of deposition, particularly near the RF coils and below the susceptor. The quartz chamber must be cleaned to prevent contamination from one run to the next. The reaction chamber cleaning procedure is as follows:

1. After each run remove the quartz chamber that was utilized and placed it in a bath of aqua regia (a mixture of 75% HCl and 25% HNO₃ by volume). The solution of aqua regia will rapidly etch the deposition within the chamber, resulting in a clean chamber for subsequent growth.
2. When the contamination is done being etched by the aqua regia (the deposits have been dissolved) remove the chamber from the acid solution. Rinse the outside of the chamber to clean off any remaining aqua regia with RO/DI H₂O.
3. Clean the left over silicon grease from the base of the chamber and the inlets with hexane.
4. Rinse the inside of the chamber with RO/DI H₂O to clean out any remaining aqua regia. Be sure to fill the inside of the chamber full of water to be sure all the aqua regia is removed. Aqua regia gives off a vapor that will adhere to the quartz unless solvated in H₂O.
5. Rinse the inside of the chamber with methanol to displace any residual water.
6. Dry the chamber with nitrogen.
7. Perform a chamber bake utilizing the Hejet heat gun to evaporate any H₂O vapor that may be desorbed on the quartz.

This process is typically done just prior to substrate preparation. The chamber is allowed to bake with the Hejet while substrate preparation is occurring. After substrate preparation, put new silicon vacuum grease on the inlet tubes and base of the reaction chamber to form vacuum seals with the ultra torr O-rings.

4.5 Film Growth

The system operation for growth is fully computer automated. The desired recipe (the code to control the system during a run) is loaded. There are 4 main steps in the growth of any thin film. They are bake-out/purge, nucleation, bulk growth and termination.
4.5.1 Film Growth: Bake-Out/Purge

At this point the substrate has been solvent cleaned and etched. However, a thin oxide may have formed on the surface in the process of loading it into the reaction chamber. Additionally, water vapor may be adhered to any surface within the reaction chamber. To purge the reaction chamber of these oxides, H₂O vapor and oxygen a bake-out and purge procedure is utilized. At the onset of growth, a pump-purge procedure is started to purge out any oxygen and replace it with nitrogen. This pump-purge procedure is 20 cycles and greatly reduces the amount of oxygen in the reaction chamber. The pump-purge procedure is followed by a 15 minute steady purge which is utilized to further purge the reactor lines. Following the steady purge, the susceptor is heated to 700°C under an overpressure of TBAs to prevent any arsenic desorption. The temperature is held at 700° for 15 mins to bake off any oxide or residual H₂O vapor. At this point the substrate and reaction chamber are ready for deposition.

4.5.2 Film Growth: Nucleation

Nucleation is similar for all growth runs. The temperature of the substrate is ramped down from 700°C to 640°C under an overpressure of TBAs to prevent any arsenic desorption. Once the desired temperature is reached the TMGa is introduced into the reaction chamber. A 750-1000Å thick layer of GaAs is deposited with the appropriate doping conditions. This layer is termed the “buffer” layer.

4.5.3 Film Growth: Bulk

Once the buffer layer epitaxy is complete, the gas composition and temperature are changed for the growth of interest. Over 1200 individual epitaxial runs were performed during the course of this research. With respect to the structures of interest in this research, growth conditions can be divided into four categories: bulk calibrations, photovoltaic devices, MQW structures and tunnel junctions. MQW growth will be discussed in more detail of chapter 6 while tunnel junctions will be covered in chapter 8. The remainder of this section will deal exclusively with bulk calibrations. Nevertheless, all growth was
accomplished with a reactor pressure of 200 torr and susceptor rotation of 120 rotations per minute (RPM).

A series of bulk calibrations were grown for the following ternary alloys, the application of each is presented in parenthesis: InGaAs (MQW), GaAsP (MQW), AlGaAs (device window). Calibration curves for InGaAs and GaAsP can be found in Fig. 4-8 and 4-9, respectively. A more in depth look at GaAsP calibrations and growth is presented in chapter 6. In addition to calibration curve generation for ternary alloys, calibration curves were also generated for the following dopants, the application of each is presented in parenthesis: GaAs:Si (devices), GaAs:Zn (devices), GaAs:C (devices), InGaP:Te (tunnel junction) and AlGaAs:C (tunnel junction). The calibration curves for each are presented in Fig. 4-10, 4-11, 4-12, 4-13 and 4-14, respectively. The flow rates are given in µmol/min, a more all-encompassing unit for flow rate as compared to standard cubic centimeter per min (SCCM). The conversion from SCCM to µmol/min is presented in the following section.

4.5.3.1 Micromolar Flow Rate Determination

Micromolar (µmolar) flow rate has been used almost exclusively in this dissertation as a way to greatly simplify the flow parameters under which the growth was accomplished. In this manner, bubbler temperature, flow rate and dilution can all be accounted for in one term. Thus, it is important to understand how the µmolar flow rates were calculated for both bath-based sources and dilute compressed gas sources contained in aluminum cylinders.

4.5.3.1.1 µmolar Flow Rate Determination: Bubbler Sources

The first step in determining the µmolar flow rate of a bubbler source is to determine its vapor pressure. For this, one must first consider how the pressure of a compound relates to the Gibb’s free energy of the compound:

\[ \ln(P) = \frac{-\Delta G}{RT} \]  \[4-1\]

where \( P \) is the partial pressure, \( \Delta G \) is the change is Gibb’s free energy, \( R \) is the Gas constant and \( T \) is the temperature of the compound. Relating 4-1 to the Entropy and Enthalpy of the compound through:

\[ \Delta G = -\Delta H - T\Delta S, \]  \[4-2\]
where $\Delta H$ is the change in enthalpy and $\Delta S$ is the change in entropy results in the following relationship:

$$\ln(P) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}. \quad [4-3]$$

Through defining the enthalpy and entropy terms as:

$$\frac{-\Delta H}{RT} = A \quad \text{and} \quad \frac{\Delta S}{R} = B, \quad [4-4]$$

and converting 4-3 into log form, the following equation is obtained:

$$\log(P) = B - \frac{A}{T}. \quad [4-5]$$

The values of $B$ and $A$ used to calculate the vapor pressure of the metalorganic sources are presented on the vapor pressure figures. These values result in vapor pressure with units of torr.

Once the vapor pressure of the compound has been determined, the Ideal Gas Law can be rearranged to give:

$$n = \frac{P_{\text{Fraction}}V}{RT} \times 10^6, \quad [4-6]$$

where $P_{\text{Fraction}}$ is the vapor pressure fraction of the source to the total pressure of the bubbler, $V$ is the flow rate in standard liters per minute (SLM), $T$ is the absolute temperature, $R$ is the gas constant and $n$ is the μmolar flow rate per minute.

4.5.3.1.1 μmolar Flow Rate Determination: Dilute Compressed Gas Source

The determination of μmolar flow rate from dilute zoo tank sources is fairly straightforward. First, the vapor fraction, $v_{\text{Fraction}}$, of the source must be determined. This value can be found on the source tank and is typically given in values of parts per million (PPM). However, even for most applications, this dilution is still not enough to obtain the desired levels for MOCVD growth. As such, these sources will also go through dilution manifolds which are comprised of a source mass flow controller and a dilution mass flow controller. Thus, the determination of the fraction of this mixture, $M_{\text{Fraction}}$, resulting from the dilution manifold must be determined. This is accomplished though the following equation:

$$M_{\text{Fraction}} = \frac{v_{\text{Fraction}}x_{\text{Source}}}{f_{\text{Source}}x_{\text{Dilution}}} = \frac{v_{\text{Fraction}}x_{\text{Source}}}{f_{\text{Total}}}, \quad [4-7]$$
where $f_{Source}$ is the flow of the source through the source mass flow controller and $f_{Dilution}$ is the flow of the dilution gas through the dilution mass flow controller. Occasionally, there may be multiple dilution manifolds on a zoo tank source. When this is the case, equation 4-7 will be used once for each dilution manifold. Once $M_{Fraction}$ has been determined, µmolar flow rate can be determined. Prior to injection into either the run or vent line, the diluted mixture will pass through a system mass flow controller. This is the last variable in determining the µmolar flow rate. The µmolar flow rate can be calculated through:

$$n = \frac{M_{Fraction} \times f_{System}}{22.4} \times 10^6,$$

where $f_{System}$ is the flow through the final, system mass flow controller in standard liters per minute (SLM), 22.4 is the number of liters one mole of a gas occupies at standard temperature and pressure (STP), and $n$ is the µmolar flow rate per minute.

4.5.4 Film Growth: Termination

For many growth structures a GaAs cap is grown as either a contact layer or to prevent some of the epitaxial films from reacting with the atmosphere or in the case of devices, both. Upon finishing the growth, the substrate temperature is lowered to 400°C before the overpressure of TBAs is turned off to prevent arsenic desorption. The reaction chamber is again put through a pump-purge cycle similar to that which starts a growth run, however this is only 10 cycles with the purpose of purging the arsenic and potential phosphorus from the growth chamber and exhaust lines.
Table 4-1: Pros and Cons of Various Growth Methods

<table>
<thead>
<tr>
<th>Growth Technique</th>
<th>Weaknesses</th>
<th>Strengths</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOCVD</td>
<td>Expensive Sources</td>
<td>Very flexible</td>
</tr>
<tr>
<td></td>
<td>Many Parameters to Control</td>
<td>Best for Industrial Applications</td>
</tr>
<tr>
<td></td>
<td>Hazardous Sources</td>
<td>High Purity</td>
</tr>
<tr>
<td>MBE</td>
<td>As/P are Difficult</td>
<td>Simple</td>
</tr>
<tr>
<td></td>
<td>Expensive</td>
<td>Very Abrupt Interfaces</td>
</tr>
<tr>
<td></td>
<td>Very Low Throughput</td>
<td>In-situ Monitoring</td>
</tr>
<tr>
<td>LPE</td>
<td>Scaling Issues</td>
<td>Simple</td>
</tr>
<tr>
<td></td>
<td>Uniformity Issues</td>
<td>High Purity</td>
</tr>
<tr>
<td>HVPE</td>
<td>No Al Compounds</td>
<td>Great for Industrial Applications</td>
</tr>
<tr>
<td></td>
<td>Hazardous Sources</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Difficult to Control</td>
<td>Well Developed</td>
</tr>
</tbody>
</table>
Table 4-2: Metal-organic Precursors Utilized

<table>
<thead>
<tr>
<th>Metal-organic Precursor</th>
<th>Chemical Equation</th>
<th>Disadvantage</th>
<th>Advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMGa, Group III</td>
<td>(CH₃)₃Ga</td>
<td>C Contamination</td>
<td>Liquid, Good Vapor Pressure</td>
</tr>
<tr>
<td>TMIn, Group III</td>
<td>(CH₃)₃In</td>
<td>C Contamination, Solid</td>
<td>Good Vapor Pressure, Also Exists as a Liquid</td>
</tr>
<tr>
<td>TMAI, Group III</td>
<td>(CH₃)₃Al</td>
<td>C Background Contamination, O Deep Levels</td>
<td>Liquid, Good Vapor Pressure</td>
</tr>
<tr>
<td>TBA, Group V</td>
<td>(C₄H₉)AsH₂</td>
<td>Expensive</td>
<td>Liquid, Good Vapor Pressure, Low C Background, Low Pyrolysis Temp.</td>
</tr>
<tr>
<td>TBP, Group V</td>
<td>(C₄H₉)PH₂</td>
<td>Expensive</td>
<td>Liquid, Good Vapor Pressure, Low C Background, Low Pyrolysis Temp.</td>
</tr>
<tr>
<td>DMZn, p-dopant</td>
<td>(CH₃)₂Zn</td>
<td>Zn Diffusion is High</td>
<td>Does not Etch</td>
</tr>
<tr>
<td>CBr₄, p-dopant</td>
<td>CBr₄</td>
<td>Ozone Depleting Etches</td>
<td>C Diffusion is Low</td>
</tr>
<tr>
<td>Disilane, n-dopant</td>
<td>Si₂H₆</td>
<td>Flammable</td>
<td>Good Doping Uniformity</td>
</tr>
</tbody>
</table>
Figure 4-1: The general schematic of a metal-organic precursor bubbler.
Figure 4-2: The vapor pressure curves for column III metal-organic precursors utilized in this research: TMAI, TMGa and TMIn.
Figure 4-3: The vapor pressure curves for column V metal-organic precursors utilized in this research: TBP and TBAs.
Figure 4-4: The vapor pressure curves for dopant metal-organic precursors utilized in this research: CBr₄ and DeTe.
Figure 4-5: Run/Vent manifold utilized in switching sources to and from the reactor.
Figure 4-6: Handmade reaction chamber utilized for all growth.
Figure 4-7: Depiction of the atomic diffusion on the surface of an (A) on axis substrate with no growth steps and (B) off-axis substrate with growth steps.
Figure 4-8: Calibration curve for In$_x$Ga$_{1-x}$As as a function of TMIn flux.

Growth Conditions:
1.95 μmol/min TMGa
57.4 μmol/min TBAs
575°C Temperature
Figure 4-9: Calibration curve for GaAs$_{1-y}$P$_y$ as a function of TBAs flux.
Figure 4-10: Calibration curve for GaAs:Si carrier concentration as a function of Disilane flux.
Figure 4-11: Calibration curve for GaAs:Zn carrier concentration as a function of DMZn flux.
Figure 4-12: Calibration curve for GaAs:C carrier concentration as a function of CBr$_4$ flux.
Figure 4-13: Calibration curve for InGaP:Te carrier concentration as a function of DETe flux.

Growth Conditions:
3.91 μmol/min TMGa
153 μmol/min TBAs
580°C Temperature
Figure 4-14: Calibration curve for AlGaAs:C carrier concentration as a function of growth temperature.
CHAPTER 5: Materials Characterization

5.1 Characterization

Characterization of any epitaxial film is imperative to understanding the effects of the growth parameters. Growth parameters primarily include temperature, source flux and pressure. Using the acquired characterization data, growth conditions can be adjusted for optimal results. There are many different tools utilized in materials characterization. Many of which will be discussed in the following sections. Of special note, many of these techniques are non-destructive, making them ideal for materials characterization prior to device fabrication.

5.1.1 Optical Microscopy

The first step in epitaxial characterization is the utilization of optical microscopy to observe the morphology of the specimen. To observe very small surface features, Nomarski differential interference contrast is necessary. An ideal specimen should appear mirror-like and featureless at magnifications ranging from 10× to 200×, indicative of well prepared and grown films (Fig. 5-1a). Typical observations include: particle debris arising from an improper cleaning procedure or gas-phase reactions (Fig. 5-1b); a hazy-like appearance resulting from poor substrate blow-off technique or exposure to air during the cleaning procedure (Fig. 5-1c); a granular morphology resulting from improper growth temperatures (Fig. 5-1d); and a characteristic cross-hatching morphology that results from either tensile or compressive relaxation of the epitaxial film (Fig. 5-1e and f, respectively).

Due to the different morphologies produced via tensile or compressive relaxation, optical microscopy is a very useful tool in determining if stress balance conditions were achieved during MQW growth. The lattice misfit dislocations in the materials of interest for this research are inclined at 60° along two orthogonal <110> directions. Compressive relaxation results in the appearance of continuous misfit lines in both directions while tensile relaxation results in the appearance of continuous misfit lines in one direction but discontinuous misfit lines in the other. A stress balanced MQW, such that the compressive
strain and tensile strain are maintained, will result in an epitaxial film which is featureless, similar to Fig. 5-1a.

5.1.2 X-Ray Diffraction

X-Ray diffraction (XRD) is a technique that allows one to analyze the crystalline structure of a material. X-rays interact and are scattered by atoms. Due to the periodicity of the atomic lattice, strong constructive interference will only occur at specific angles, known as Bragg reflections. These Bragg reflections will only occur at angles which satisfy Bragg’s law:

\[ n\lambda = 2d_{hkl}\sin\theta, \]  

[5-1]

where \( \lambda \) is the x-ray wavelength, \( d \) is the spacing between crystalline planes, and \( \theta \) is the diffraction or Bragg angle. For a more detailed background and understanding of x-ray crystallography refer to the literature.\(^3\)\(^-\)\(^5\) XRD was used to determine the ternary alloy composition of bulk samples, MQW periodicity and layer thicknesses and to evaluate the degree to which the MQW structures were balanced.

5.1.2.1 X-Ray Diffraction: Bulk Measurements for Alloy Calibration

The basic measurement obtained through XRD is that of the 2\( \theta \)-\( \theta \), performed using a Rigaku Geigerflex diffractometer, or the 2\( \theta \)-\( \omega \), performed using a 3-axis Philips PANalytical X’Pert system. Both machines utilize a Cu anode and produce K\( \alpha \) radiation (1.541838 Å). However, the Philips uses either a four-bounce Ge (220) crystal or a four-bounce Ge(440) coupled with a parabolic mirror, termed a hybrid monochromator, to select only for Cu K\( \alpha \)1 energy transition (1.540562 Å). The scans obtained from these machines were used to determine the composition of the ternary alloys through the use of Vegard’s law:

\[ a_{Alloy} = a_{Binary_1}(x) + a_{Binary_2}(1-x), \]  

[5-2]

where \( a \) is lattice constant of the corresponding material and \( x \) is the composition of the alloy in terms of the binary 1 endpoint. Lattice constant, \( a \), is related to the spacing between crystalline planes, \( d \), of equation 5-1 through the following equation:

\[ d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}, \]  

[5-3]
where \( h, k \) and \( l \) are the miller indices for the plane of interest, typically the (004), (224) or (115) for GaAs. As can be seen, Vegard’s Law assumes a linear relationship between the binary end points and the lattice parameters of the alloy comprised thereof for solid solutions. It should be noted that Vegard’s Law assumes there is no strain in the alloy and that it has relaxed fully. It is possible to take into account the effect of strain on the bulk calibrations; however, most films are grown well past the point of 100% relaxation, allowing for Vegard’s law to be utilized un-modified. Typical \( \text{In}_x\text{Ga}_{1-x}\text{As}, \text{GaAs}_{1-y}\text{P}_y \) and \( \text{Al}_x\text{Ga}_{1-x}\text{As} \) calibration 2\( \theta \)-\( \theta \) spectra are presented in Fig. 5-2a, b and c, respectively. Of interest with these three examples is the fact that AlAs has a very small lattice mismatch with GaAs (~0.1%). As such, it is very difficult to grow AlGaAs alloys to 100% relaxation. Due to this, fully strained films of AlGaAs are grown for calibration purposes. As such, the peak splitting between the substrate and alloy will be changed by a factor of:

\[
\Delta2\theta_{Actual} = \frac{1-v}{1+v} \Delta2\theta_{100\% Strained},
\]

where \( v \) is the Poisson’s ratio of the material, \( \Delta2\theta_{Actual} \) is the substrate/alloy peak splitting for relaxed films and \( \Delta2\theta_{100\% Strained} \) is the substrate/peak splitting for 100% strained films. For the purposes of this research, all AlGaAs alloys are assumed to have a Poisson’s ratio of 0.31. For a more in-depth look at analyzing AlGaAs alloys through XRD please refer to the literature.6-7

5.1.2.2 X-Ray Diffraction: MQW Analysis

The most powerful tool for determining the periodicity, layer thicknesses and degree of stress balance within the MQW is that of XRD. However, to fully appreciate the data obtained from XRD pertaining to the MQW structure, one must understand the incredible pressures acting in the thin films and how they affect the lattice of the thin films. As such, the following sections are on the stress and strain calculations for the MQW structure followed by MQW XRD analysis.
5.1.2.2.1 MQW Stress and Strain

There are two primary types of stress in thin films. Intrinsic stress arises from defects in the material. Extrinsic stress in a thin film arises from its adhesion to the substrate. Extrinsic stress in a thin film can be due to thermal expansion, lattice/substrate misfit or possibly chemical reactions. These reactions take place on the substrate growth surface resulting in the formation of intermetallic compounds at the substrate/thin film interface which is still coherent to the film, but ultimately has a slightly different lattice constant.

While there is some hydrostatic stress in thin films at the growth steps of the substrate/thin film interface, the bulk of the stress is biaxial. As such, any hydrostatic stress will be ignored for this dissertation to greatly simplify the calculations needed to determine the thin film stress and strain. For biaxial stress, the stresses act along two principal axes in the plane of the film and the third direction, that which is perpendicular to the surface of the substrate, is stress free. Biaxial stress is expressed as a three-dimensional isotropic system, which works very well for zinc-blend structures. The stress and strain for this three-dimensional isotropic system are related by the following equations:

\[
\varepsilon_x = \frac{1}{Y}[\sigma_x - \nu(\sigma_y + \sigma_z)], \tag{5-5}
\]

\[
\varepsilon_y = \frac{1}{Y}[\sigma_y - \nu(\sigma_x + \sigma_z)], \tag{5-6}
\]

\[
\varepsilon_z = \frac{1}{Y}[\sigma_z - \nu(\sigma_y + \sigma_x)], \tag{5-7}
\]

where \(\varepsilon\) is strain, \(\sigma\) is stress, \(Y\) is the Young’s modulus and \(\nu\) is the Poisson’s ratio. As previously mentioned, there is no stress in the direction perpendicular to the growth plane, so \(\sigma_z = 0\). Additionally, for isotropic cubic structures the stresses in the x and y directions are equal, \(\sigma_x = \sigma_y\) now defined as \(\sigma_{xy}\).

\[
\varepsilon_x = \frac{\sigma_{xy}}{Y}(1 - \nu), \tag{5-8}
\]

\[
\varepsilon_y = \frac{\sigma_{xy}}{Y}(1 - \nu), \tag{5-9}
\]

\[
\varepsilon_z = \frac{-\nu}{Y}(2\sigma_{xy}), \tag{5-10}
\]

Thus the strain in both the x and y directions are the same. The parameters of interest for the binary endpoints of the ternary alloys are presented in Table 5-1.
Strain in the x and y direction is calculated from the lattice parameters of the film and substrate through the following relationship:

$$\varepsilon_{\text{alloy,strained}} = \frac{a_{\text{substrate}} - a_{\text{alloy,relaxed}}}{a_{\text{alloy,relaxed}}}$$ \hspace{1cm} [5-11]

where $a_{\text{substrate}}$ is the GaAs lattice constant of 5.65Å and $a_{\text{alloy,relaxed}}$ is the lattice constant of the relaxed ternary alloy of interest. A visualization of the strain for both a compressive and tensile strain is presented in Fig. 5-3. As can be seen, the alloy must conform to the in-plane lattice constant of the substrate. $a_{\text{alloy,relaxed}}$ is determined via a linear interpolation of the binary endpoints. Graphical representations of the linear interpolations for the Young’s modulus, Poisson’s ratio and lattice constant of both the InGaAs and GaAsP alloys are presented in Fig. 5-4, 5-5, and 5-6, respectively. With this data, it is possible to calculate the stress in the thin film layers. A graphical representation of the stress calculation for both InGaAs and GaAsP alloys is presented in Fig. 5-7. By definition of the equations utilized, compressive strain will result in negative stress values while tensile strain will result in positive stress values. The most highly stressed layer utilized in this research is that of the GaAs$_{0.2}$P$_{0.8}$ barrier of the MQW structures. These layers have a stress of ~4.2 GPa. To put this value into better perspective, a list of pressures for various situations is presented in Table 5-2.

5.1.2.2 n$_0$ Determination, Periodicity and Layer Thickness

XRD analysis is possible because X-rays interact with the periodic structure of a crystal lattice. Likewise, the periodic structure of the MQW will also interact with X-rays resulting in a periodic, or Pendelosung fringes, XRD signature as presented in Fig. 5-9. With respect to the MQW structure stress balance, the most important characterization technique is that of the n$_0$ determination via XRD 2θ-θ and HRXRD 2θ-ω scans. The n$_0$ peak for a MQW structure is a representation of the average lattice constant for that MQW structure. When strained materials comprising a MQW structure have the same Poisson’s ratios, the stresses in the materials will be balanced when the average lattice constant of the MQW comprised of these materials gives a Bragg reflection exactly that of the substrate. However, when there is a difference in Poisson’s ratios, as there is with InGaAs and GaAsP, the average lattice
parameter will be dictated to a greater degree by the material with the larger Poisson’s ratio, in this example InGaAs. Thus, the Bragg condition will be satisfied in accordance to the difference in Poisson’s ratio, and the $n_0$ peak will reside on the side for which the material has the largest Poisson’s ratio. For a MQW structure composed of InGaAs wells and GaAsP barriers, the $n_0$ peak will always reside on the low side of the GaAs substrate peak when stresses are properly balanced. Thus, aside from visual inspection via optical microscopy, XRD 2θ-θ and HRXRD 2θ-ω scans are the most important tool for determining MQW stress balanced conditions. It should be noted that this is in lieu of in situ monitoring systems such as curvature monitoring which would be the best way of determining stress balance conditions.

It is not always easy to determine where the $n_0$ peak is located in an XRD scan of a sample. The best way to determine the location of the $n_0$ peak is through modeling of the MQW structure via Bede RADS or Philips PANalytical X’pert modeling software. The bulk of modeling for this research was accomplished using the Philips PANalytical X’pert software. The software is very useful in modeling both simple and complex structures. The program calculates high resolution rocking curves for epitaxial crystal structures using the fundamental X-ray scattering equations of dynamical diffraction.

To use the modeling software to determine the location of the $n_0$ peak, the first step is to analyze the obtained MQW XRD scan. It is best to assume that the compositions of the alloys within the MQW structure are the same as those obtained in bulk growth. The periodicity of the MQW structure can be calculated by modifying Bragg’s law to:

$$\Lambda = \frac{(n_i-n_j)\lambda}{2(sin\omega_i-sin\omega_j)}, \quad [5-12]$$

where $n_i$ and $n_j$ are satellite peaks with positions of $\omega_i$ and $\omega_j$, respectively. $\lambda$ is the wavelength of the x-ray source (1.54nm for Cu) and $\Lambda$ is the periodicity of the repeating MQW units. Once $\Lambda$ is determined it is possible to calculate the thickness of each layer within the repeating MQW unit. One thing that must always be considered is that the growth rate is determined solely by the column-III species as they are the limiting reagents. As such, the growth rate of the InGaAs wells is higher than that of the other materials as the TMGa
flow is not changed at any point within the MQW growth. This has been presented graphically in Fig. 5-8. Due to this, an effective growth time must be calculated for the InGaAs layers. This calculation is done through the following equation:

$$t_{In, effective} = \frac{t_{In, actual}}{1 - x_{In, composition}}.$$ [5-13]

After the effective time for the wells has been determined, the time to grow a MQW unit can be calculated by adding the other layer growth times to that of the effective indium growth time. Dividing $\Delta t$ by this unit time will give the normalized growth rate. The thicknesses for each layer can be determined by multiplying this normalized growth rate by the growth time for each layer, the effective growth time for the wells. An example of this calculation is presented in Fig. 5-9. The data obtained from the XRD presented in Fig. 5-9, in addition to the growth times from the run, are tabulated in Table 5-3. With the bulk calibrations and the layer thicknesses calculated, it is possible to model the intended structure.

For the most part the model will not match the actual XRD signature. However, the modeled satellite peaks should be similar to those obtained from the actual XRD. As an example, the model for the actual XRD of Fig. 5-9 is presented in Fig. 5-10. To determine which peak is the $n_0$ peak within this signature, another model is needed in which the ratio of well/barrier stays constant, but the periodicity changes. All of the satellite peaks will move away from the $n_0$ peak. This peak can then be matched to that of the actual XRD data. In the example presented here, the $n_0$ peak is that which is buried under the GaAs substrate peak for the obtained MQW signature. Modeling should be undertaken each time a MQW structure is grown and characterized via XRD to ensure the $n_0$ peak, and the stress balance, is determined.

5.1.3 Photoluminescence

Photoluminescence (PL) is a useful technique for characterizing the optical properties of epitaxial materials and has been utilized exclusively on MQW structures for this research. Electron-hole pairs (EHPs) are created in the MQW structures by exposing the samples to photons with energy greater than the bandgap of the material. After carrier excitation, the carriers decay and recombine through radiative recombination mechanisms generating
photons with energy equivalent to that of the material bandgap. In this manner, MQW bandedge can be determined without the need of producing devices, greatly increasing the rate at which MQW bandedge trends could be analyzed.

The bandedge of the MQW is greatly affected by the degree to which the carriers are confined in the wells. As the barriers get taller (in energy terms) there is more quantum confinement. Additionally, as the wells get thicker there is more quantum confinement. Thus, PL can be a great tool in mapping the thickness of the MQW structure and looking at the growth uniformity across a sample. An example of this is presented in Fig. 5-11.

Not conducted in the research presented herein, PL can also be used to determine minority carrier lifetime. Short pulses of light are used to generate EHPs. The time it takes these EHPs to return to equilibrium are measured, a process known as time-resolved PL (TRPL). It is regretful that TRPL has not yet been performed on any of the MQW structures presented in this research as good minority carrier lifetime is important for proper device performance. With poor minority carrier lifetime, carriers will recombine in the intrinsic region of the solar cell before they can contribute to a photocurrent. In our devices, the intrinsic region is the MQW structure. To this point there is no evidence that minority carrier transport through the MQW is affected by poor carrier lifetime in the wells.

5.1.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is the best method for measuring the small features of the MQW structure. These features include the ordering, defects, strain, compositional gradients and layer thickness. However, TEM sample preparation can be tedious and time consuming. As such, TEM is used as a supporting analytical technique rather than a primary technique. For further understanding of the specifics related to TEM, there are several good resources.

Typical TEM samples prepared were done so in cross-section. The procedure for prepping these samples is presented below.

1. Fix an epitaxial sample to a glass slide growth side down with clear wax (Crystalbond 509-3). A hotplate is needed for this.
2. Using a diamond blade, saw the affixed sample into 2 mm × 2 mm sections using a sample prep saw. The TechCut 4 produced by Allied High Tech was used for this research. Four rotations of the micrometer is equivalent to 2 mm. Sample rotation of 90° will be required to obtain 2 mm × 2 mm sections. Multiple sections will be needed for cross-sectional TEM sample prep.

3. Remove the 2 mm × 2 mm sections from the glass slide using a hotplate. Wash the squares first with acetone to dissolve the remaining clear wax. Sonication may be needed for ~5-10 mins.

4. Follow the acetone sonic bath with isopropyl-OH and sonicate for five mins. Pour the now cleaned 2 mm × 2 mm sections onto filter paper and allow the isopropyl-OH to evaporate.

5. Apply an adhesive (Micro-Measurements M-Bond 610) to the epitaxial face of one 2 mm × 2 mm section and place the epitaxial face of another section onto the adhesive face creating a structure similar to that of Fig. 5-12. Clamp the structure together and allow the adhesive to dry. Drying instructions for the Micro-Measurements M-Bond can be found in the literature.14

6. After the section stack adhesive has cured the stack can be cut in half to yield two 2 mm × 1 mm section stacks. Again, use the diamond blade and saw from step 2.

7. The next step of the process is preparation of a quartz stub onto which the 2 mm × 1 mm section stacks will be placed. It is of the utmost importance that these stubs be parallel to the plan used in polishing the TEM polishing. As such, the quartz stub is made parallel to the platen by using sequentially 9 µm, 6 µm and 3 µm diamond lapping films (DLF). Upon using the 3 µm film, the quartz stub should appear very smooth and free of scratches under a stereo microscope.

8. After stub preparation the 2 mm × 1 mm section stacks are affixed to the stub using clear wax such that the interface created by the adhesive is perpendicular to both the front and prepared face of the stub.

9. Bulk material is removed from the stacks use 9 µm DLF followed by 3 µm DLF with platen rotation of 100 rpm with a flow of H₂O to provide both lubrication and sequester any particles that are created. The load used for this process can be adjusted. It was found that 100g worked well for GaAs based materials. The sample should have a thickness of ~350-450 µm and the specimen should be inspected often to ensure material removal is proceeding accordingly. NOTE: If making TEM samples from epitaxial films grown on sapphire substrates, bulk material removal should be started with 30 µm DLF and be followed with 15 µm, 9 µm, 6 µm and 3 µm DLF.

10. Follow bulk material removal with 1 µm DLF at 80 rpm but DO NOT USE H₂O HERE! Instead use GreenLube polishing lubricant. While not a major issue at this step, the surface tension of H₂O can cause the sample to be pulled into the DLF and crack.

11. Follow 1 µm DLF polishing with 0.1 µm DLF at 50 rpm. Again, DO NOT USE H₂O HERE, but instead, use GreenLube.
12. The final polish for the first side is a 0.02µm colloidal silica suspension utilizing a platen with a felt surface. Platen rotation is set to 100rpm with H₂O at edge of platen. The capillary action of the felt will bring enough water to the center of the platen. The specimen is lowered so that it is just creating a buildup of colloidal silica/H₂O on its leading edge. The specimen is polished for 2mins at this step. Upon completion of this polishing step the specimen is cleaned using Micro Organic soap on the felt platen. This soap will remove any remaining silica from the specimen. The specimen should be ~350-500µm at this stage of the process.

13. The sample is removed from the quartz stub, flipped and reattached with clear wax for the second side polish process. The specimen should be situated such that is sticks out slightly from the front face of the quartz stub for proper wedge formation.

14. Begin polish of second side with 9µm at 50rpm till a thickness of 100µm is obtained.

15. Follow 9µm DLF with 3µm DLF till a thickness of ~35µm is obtained. The ultimate TEM sample thickness is important as some TEM sample holders will not work with thick samples.

16. Once the specimen is the thickness of a TEM sample grid (~35µm), the wedge is started. The wedge is set using the left micrometer and is adjusted to an angle of 2 degrees. One rotation of the micrometer is one degree. Please refer to the Allied High Tech MultiPrep user manual for further details.

17. Use 1µm DLF at 50rpm to wedge while NOT POLISHING THE STUB. DO NOT USE H₂O HERE but instead use GreenLube. Check often to determine if the wedge is forming properly. Proper wedge formation will result in the appearance of thickness fringes appearing at the leading edge of the specimen.

18. Once thickness fringes begin to appear, use 0.1µm DLF at 30rpm and a load of 0-50g to remove the polish lines and debris from the previous DLF. DO NOT USE H₂O but instead use GreenLube.

19. Upon the formation of decent thickness fringes, and example of which is presented in Fig. 5-13, use the felt platen along with 0.02 colloidal silica suspension at 100rpm as in step 12.

20. Clean the TEM specimen with soap before each inspection. Inspect often to ensure the thickness fringes improve.

21. TEM sample prep is finished when good, uniform thickness fringes are observed.

22. The TEM grid must now be applied to the prepared TEM specimen. With the specimen still affixed to the quartz stud apply a very small amount of M-bond to the thick part of a TEM grid. Carefully apply the TEM grid, M-bond side down, onto the specimen such that the M-bond makes good contact with the samples thickest portion and the thinnest portion of the TEM specimen is located nicely in the center of the TEM grid.

23. Allow the TEM grid/specimen/stud combo to cure overnight at the very minimum.

24. Place the TEM grid/specimen/stud combo into a petri dish lined with filter paper. Dissolve the CrystalBond in acetone and remove the TEM grid/specimen from the acetone as soon as
it falls from the quartz stud immediately placing it in a petri dish of isopropyl-OH. It is easiest to move the TEM grid/specimen combo by using the filter paper.

25. Allow the TEM grid/specimen combo to sit in the isopropyl-OH until all the isopropyl-OH evaporates.

26. At this point the TEM specimen can either be placed in an Ion-mill for further polishing or, provided the thickness fringes are good and uniform, a TEM for analysis.

The TEM measurements were performed on up to three TEMs. Each of these TEMs have their own inherent strengths and weaknesses. The JEOL-2000 is a great machine for general analysis, g.b defect analysis and EDS. The JEOL-2010 is great for high resolution TEM (HRTEM) and scanning TEM (STEM). The FEI Titan 80-300 STEM is an advanced analytical workstation allowing sub-angstrom resolution and atomic level energy dispersive spectroscopy (EDS) analysis.

5.1.5 Hall Effect

Basic electrical characteristics such as resistivity, mobility, carrier concentration and carrier type were determined via Hall measurements in the van der Pauw configuration.\textsuperscript{15} Indium dots are annealed in a nitrogen environment on the surface of 6mm×6mm samples to create ohmic contacts. Gold wires are then soldered to the indium dots for connection with an external circuit. Current and voltage is provided by a Keithly source interfaced with an Agilent multiplexer. A 3 kGauss magnetic field is created with an electromagnet. Data is collected through a computer program and carried out at room temperature. All films characterized through Hall measurements were grown on semi-insulating substrates.

Table 5-1: Materials Parameters for Binary Compounds of Interest

<table>
<thead>
<tr>
<th>Constants</th>
<th>Binary Material</th>
<th>Young’s Modulus (GPa)</th>
<th>Poisson’s Ratio</th>
<th>Lattice Constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GaAs</td>
<td>85.5</td>
<td>0.31</td>
<td>5.65</td>
</tr>
<tr>
<td></td>
<td>InAs</td>
<td>51.4</td>
<td>0.35</td>
<td>6.06</td>
</tr>
<tr>
<td></td>
<td>GaP</td>
<td>103</td>
<td>0.31</td>
<td>5.45</td>
</tr>
</tbody>
</table>
Table 5-2: Pressure Values for Specific Situations

<table>
<thead>
<tr>
<th>Example</th>
<th>Pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyena bite force</td>
<td>0.078&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
<tr>
<td>Bottom of the Mariana Trench</td>
<td>0.11&lt;sup&gt;17&lt;/sup&gt;</td>
</tr>
<tr>
<td>Formation of Metamorphic Rock</td>
<td>0.15&lt;sup&gt;18&lt;/sup&gt;</td>
</tr>
<tr>
<td>GaAs&lt;sub&gt;0.3&lt;/sub&gt;P&lt;sub&gt;0.8&lt;/sub&gt; MQW Barriers</td>
<td>4.2</td>
</tr>
<tr>
<td>Diamond Formation</td>
<td>5&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>Center of the Earth</td>
<td>360&lt;sup&gt;20&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Table 5-3: Data Determined from Fig. 5-9 in Conjunction with Run Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD Periodicity</td>
<td>142Å</td>
<td>GaAs t&lt;sub&gt;growth&lt;/sub&gt;</td>
<td>8.25sec</td>
</tr>
<tr>
<td>Indium Composition</td>
<td>20%</td>
<td>Total t&lt;sub&gt;effective&lt;/sub&gt;</td>
<td>37.35sec</td>
</tr>
<tr>
<td>Indium t&lt;sub&gt;growth&lt;/sub&gt;</td>
<td>16.84sec</td>
<td>Growth Rate</td>
<td>3.80Å/sec</td>
</tr>
<tr>
<td>Indium Composition</td>
<td>20%</td>
<td>Indium Thickness</td>
<td>80Å</td>
</tr>
<tr>
<td>Indium t&lt;sub&gt;effective&lt;/sub&gt;</td>
<td>21.05sec</td>
<td>Phosphorus Thickness</td>
<td>31Å</td>
</tr>
<tr>
<td>Phosphorus t&lt;sub&gt;growth&lt;/sub&gt;</td>
<td>8.05sec</td>
<td>GaAs Thickness</td>
<td>31Å</td>
</tr>
<tr>
<td>Phosphorus Comp.</td>
<td>81%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5-1: Example morphologies for (A) a well prepared and grown featureless sample, (B) a sample with debris most likely due to poor cleaning,\textsuperscript{21} (C) haziness areas due to poor sample blow-off or exposure to air during solvent/etch procedures and typically occurs near the edge, (D) granular morphology due to a bad growth temperature, (E) misfit dislocations due to tensile relaxation\textsuperscript{21} and (F) misfit dislocations due to compressive relaxation.\textsuperscript{21}
Figure 5-2: XRD calibrations of (A) an InGaAs alloy, (B) a GaAsP alloy and (C) an AlGaAs alloy. Substrate κα1 and thin film κα1 Bragg reflections have been labeled with S and F, respectively.
Figure 5-3: Strain effects for (A) tensile strain and (B) compressive strain. Note how the lattice constants for the thin films change.
Figure 5-4: Young’s Modulus for InGaAs and GaAsP alloys.
Figure 5-5: Poisson’s ratio for InGaAs and GaAsP alloys.
Figure 5-6: Relaxed InGaAs and GaAsP alloy lattice constants.
Figure 5-7: Stress values for InGaAs and GaAsP alloys grown pseudomorphic to GaAs substrates.
Figure 5-8: Growth rate of films as a function of indium composition.
Figure 5-9: XRD (004) 2θ-θ scan of an as-grown MQW structure.
Figure 5-10: Model of the MQW from Fig. 5-9 in addition to a model of the same structure but with thicker InGaAs and GaAsP layers such that the well/barrier ratio is unchanged.
Figure 5-11: PL mapping of a MQW structure showing the non-uniformity across the wafer.
Figure 5-12: Schematic of a TEM specimen stack.
CHAPTER 6: Growth and Characterization of In\(_{x}\)Ga\(_{1-x}\)As/GaAs\(_{1-y}\)P\(_y\) Strained Layer Superlattices with high values of \(y\) (~80%) and Staggered Multi-Quantum Well Structures for Overcoming Quantum Size Effects

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6.1 Abstract

Multi-quantum well (MQW) structures, such as InGaAs/GaAsP lattice matched to GaAs, have shown great potential in absorption devices such as photodetectors and triple junction photovoltaic cells. However, until recently they have been somewhat hindered by their usage of low phosphorus GaAsP barriers. High-P composition GaAsP was developed as the barrier for InGaAs/GaAsP MQW structures, and the merits for using such a high composition of phosphorus are discussed. It is believed that these barriers represent the highest phosphorus content to date in such a structure. By using high composition GaAsP the carriers are collected via tunneling (for barriers \(\leq 30\)Å) as opposed to thermionic emission. Thus, by utilizing thin, high content GaAsP barriers one can increase the percentage of the intrinsic region in a p-i-n structure that is comprised of the InGaAs well in addition to increasing the number of periods that can be grown for a given depletion width. However, standard MQWs of this type inherently possess undesirable compressive strain and quantum size effects (QSE) that cause the optical absorption of the thin InGaAs wells to shift to higher energies relative to that of bulk InGaAs of the same composition. To circumvent these deleterious QSEs stress balanced, pseudomorphic InGaAs/GaAsP staggered MQWs were grown. Staggering was achieved by removing a portion of one well and adding it to an adjacent well. The spectral response obtained from device characterization indicated that staggering resulted in thicker InGaAs films with reduced cutoff energy. Additionally, this
data confirms that tunneling is a very effective means for carrier transport in the MQW structures.

6.2 Introduction

III–V semiconductors are useful in optoelectronic applications; however, not all desired bandgaps are available in alloys lattice matched to available substrates. This limitation can be overcome by using metamorphic and pseudomorphic structures. Metamorphic structures have issues with defects which can be alleviated, but not eliminated. Individually, pseudomorphic layers are limited by the critical layer thickness, after which relaxation occurs. This deleterious relaxation limits the total thickness of an individual pseudomorphic layer to the range of a few nanometers to a few tens of nanometers. To avoid relaxation, many pseudomorphic layers can be grown by balancing compressive and tensile layers in a structure termed a strain balanced, multi-quantum well (MQW) structure. The concept of the strain balanced InGaAs/GaAsP MQW, lattice-matched to GaAs was developed in the 1980s, and used in several structures such as LEDs\(^1\), solar cells\(^2\) and buffer layers to reduce defects in heterostructures.\(^3\)

One application where strain balanced SLSs are particularly promising is in the InGaP/GaAs/Ge triple junction (3J) photovoltaic cell, wherein increased efficiency can be obtained by extending the absorption of the middle GaAs or top InGaP cell to longer wavelengths and improving the spectrum matching between the three subcells. The first lattice-matched strain-balanced superlattice solar cells were fabricated for solar spectrum matching in tandem cells\(^2\). After efficient InGaP/GaAs tandems were developed, QWs within the intrinsic region of a p–i–n solar cell were suggested as a means to improve spectral matching.\(^4\) An SLS system consisting of InGaAs/GaAsP has potential to improve spectrum matching of 3J PV.

The design of the SLS depends on several parameters; mainly the strain balance of the SLS, the critical layer thickness of both the individual pseudomorphic layers and the SLS as a whole and the requirement for an efficient carrier transport across the barriers in both the
conduction and valence bands. In this paper we describe the growth and characterization of the SLS using very high GaAs$_{1-y}$P$_y$ phosphorus compositions to create a high band gap barrier layer. The advantages of using high content phosphorus barriers are as follows: first, high GaP composition will allow for thicker In$_x$Ga$_{1-x}$As optical absorbing wells while maintaining strain balance conditions. Second, high GaP content will allow for thin barriers, resulting in an i-layer being comprised mainly of the InGaAs absorption layers. This will enhance the gain in $J_{sc}$ as compared to that of a GaAs cell. Third, a thin barrier (with high GaP composition) will allow carriers to be transported by tunneling as demonstrated in Fig. 6-1. It can be shown, for example, that for a SLS consisting of In$_{0.15}$Ga$_{0.85}$As/GaAs$_{0.2}$P$_{0.8}$, $>75\%$ of the i-layer is composed of the absorbing InGaAs wells while maintaining carrier transport efficiency close to 100\% via tunneling. This tunneling approach is advantageous with respect to that of other approaches that utilize thermionic emission for carrier transport $^5$. The latter approach requires thick (>200Å), low (6\% P) GaAsP content barriers which results in only $\sim$25\% of the i-layer being the InGaAs absorbing wells.

The use of thin, high content GaP barriers results in InGaAs wells which are also relatively thin (50-100Å) and the problem is compounded as one moves to higher indium compositions of InGaAs while maintaining strain balance conditions. Thus, due to these fairly thin wells, there will be an undesirable shift in the threshold energy of the absorbed photons due to quantum size effects (QSE).

To reduce the impact of the QSE, we have devised the concept of a staggered SLS.$^6$ In this system, the thickness of one well is increased at the expense of an adjacent well. The period of the staggered SLS is thus doubled for all values of $x$ and includes two wells and two barriers. However, the average zero stress balance condition remains constant. Thus, the stress in the structure was balanced for every period of two QWs. A schematic of the staggered SLS is presented in Fig. 6-2. This staggered SLS with two GaAsP barriers per period can only be implemented in a structure that utilizes thin GaAsP layers containing high composition GaP. While this staggering is expected to result in an extension of the band
edge to a longer wavelength, it is imperative that the InGaAs wells do not exceed their critical layer thickness (CLT).

This paper describes methods to achieve GaAs$_{1-y}$P$_y$ with high phosphorus composition barriers in SLS while maintaining strained balanced conditions, and presents a staggered SLS structure which can be used to minimize and avoid QSEs. This paper presents the growth conditions for GaAs$_{1-y}$P$_y$ with 0.6<y<0.8 as well as the growth of both the standard and staggered InGaAs/GaAsP SLS. Both materials and device aspects of these SLSs will be discussed.

6.3 Experimental

All growth is carried out using a MOCVD growth system utilizing a homemade reactor that allows for fast gas switching that is required for the growth of the In$_x$Ga$_{1-x}$As/GaAs$_{1-y}$P$_y$ SLS. The structures are grown on (100) GaAs substrates oriented 2° to the (110) using tertbutyl arsine (TBAs), tertbutyl phosphine (TBP), trimethyl indium (TMIn) and trimethyl gallium (TMGa). The SLS structure is grown in the temperature range of 570-600°C with a growth rate between 6-8Å/s. This growth temperature range is a compromise between the high growth temperature preferred for GaAsP growth and the relatively lower growth temperature preferred for InGaAs. The InGaAs well compositions range from 5-20% indium while the GaAsP barrier compositions range from 70-85% phosphorus for MQWs. All samples were characterized initially with optical Nomarski microscopy followed by X-ray diffraction (XRD). Optical microscopy was performed with an Olympus BX41 microscope fitted with a Nikon D3000 camera through the use of an Alexis Scientific adaptor. Optical microscopy is a very useful and easy characterization tool to determine if the MQW structure has relaxed as crosshatching can be seen for unbalanced MQW structures. The MQW structure was characterized with the use of a Philips Panalytical X’Pert to determine the MQW period, layer thicknesses and balance conditions. The nominal thickness of the GaAsP barriers for strain balanced superlattices was ~30 Å for all samples that were shown to have tunneling probabilities of about 100% 7. InGaAs well thickness was determined via the zero-stress balance method for varying indium compositions. In order to
evaluate the effect of staggering, samples with alternating thicknesses of InGaAs layers, as shown in Fig. 6-2, were grown with adjacent well thickness ratios of 1:1, 3:1 and 5.667:1. The conventional MQW device consisted of 20-40 periods of the alternating layers while the staggered MQW, by definition of its period, consisted of 10-20 periods. As a control, a standard GaAs cell lacking a MQW structure or intrinsic layer was grown.

Devices were fabricated by conventional contact photolithography as 2.5 mm × 2.5 mm etched mesas with electron beam evaporated metallization consisting of Ni/AuGe/Au n-type ohmic contacts and Ti/Pd/Ag p-type ohmic contacts. The metallization was annealed at 400 °C for 40 s. The cells were fabricated without an antireflective coating. The fabricated devices were characterized with an Oriel 1 kW solar simulator at one sun illumination (AM 1.5 filter) in order to determine the open-circuit voltage ($V_{OC}$), the short-circuit current ($I_{SC}$), and the fill factor. A Newport Cornerstone 260 ¼ m monochromator coupled with a tungsten halogen light source provided the illumination for spectral response measurements.

6.4 Results and Discussion

The phosphorus composition as it relates to the TBP flow is shown in Fig. 6-3. All TBAs and TMGa flow rates for these calibrations were 20 sccm and 2 sccm respectively with bubbler temperatures of 5.2°C and 0.0°C respectively. A substrate temperature of 600°C was used for the growth. As can be seen, the phosphorus composition reaches a saturation point for a given substrate temperature. It is near this saturation for which we observed the most reproducible growth with respect to the MQW; the reasons for this phenomenon may be explained in multiple ways. When saturated, any variations with respect to TBP bubbler temperature, TBP bubbler pressure and system pressure will be minimized within the growth itself. Additionally, we were able to obtain phosphorus compositions of 85% and higher by changing the substrate temperature. However, it was observed that with higher substrate temperature came more difficulty in obtained good quality MQWs. It is posited that due to the higher temperature, desorption of the arsenic species becomes too high for the indium wells, which result in indium and gallium droplets on the sample ruining the morphology.
These MQWs consist of InGaAs/GaAs$_{0.25}$P$_{0.75}$ and we believe this to be the highest phosphorus composition reported and used in multi-quantum well (MQW) structures. Optical microscopy can be used as a quick indication for the onset of relaxation in the MQW as the relaxation manifests itself as a characteristic cross hatch of the sample surface.

To balance the SLS, a zero-stress balance method was utilized:

$$a_{sub} = \frac{A_{In}t_{In}a_{In}^2 + A_{P}t_{P}a_{P}^2}{A_{In}t_{In}a_{In}^2 + A_{P}t_{P}a_{P}^2}$$

where $a_{sub}$, $a_{In}$, $a_{P}$ are the lattice constants of the substrate, InGaAs wells and GaAsP barriers, respectively; $t_{In}$ and $t_{P}$ are the well and barrier thicknesses, and $A_{In}$, $A_{P}$ is a stiffness parameter for the InGaAs wells and GaAsP barriers, respectively. The stiffness parameters were calculated using the elastic stiffness coefficients for each material:

$$A = C_{11} + C_{12} - \frac{2C_{12}^2}{C_{11}}$$

When dealing with ternary compounds it is assumed that the elastic coefficients, $C_{11}$ and $C_{12}$, can be linearly interpolated from the two binary materials comprising the ternary compound. However, while this is fairly accurate near the peripheries (±20% of the endpoints) of the ternary compound composition, it becomes problematic the farther one shifts from the peripheries as many ternary compounds have unknown bowing parameters that must be considered. Additionally, the zero-stress balance equation is based solely on a strain energy analysis, not taking into account any kinetic barriers. Nevertheless, balanced MQW structures have been successfully grown using this method. Fig. 6-4 reports the values obtained using this model with different InGaAs well composition thicknesses with respect to GaAs$_{0.2}$P$_{0.8}$ barrier thicknesses. The horizontal bold line represents the barrier thickness limit for tunneling of the minority carriers. Fig. 6-4 is used as a guide line for the strain adjustments for the different MWQ compositions studied in this work.

In addition to helping determine the quality of the MQW, XRD was also used to determine the thickness of the periods in the MQW structure and to verify that zero stress conditions were met. The periodic satellite fringes were used to determine the thickness of a period in the MQW by:
where $\theta_{n\pm1}$ or $\theta_n$ is the Bragg angle for the $n\pm1$ or $n$ satellite fringe, $\lambda$ is the source wavelength and $t$ is the thickness of each period and is comprised of the In wells, phosphorus barriers and GaAs transition layers.

The XRD analysis for three samples is presented in Fig. 6-5. Fig. 6-5(a) is the XRD data as collected from a normal MQW consisting of $\text{In}_{0.15}\text{Ga}_{0.85}\text{As}/\text{GaAs}_{0.2}\text{P}_{0.8}$. The peaks are well defined with relatively narrow full width half maxima (FWHM) values. There appears to be some broadening of the peaks on the indium side ($<66.04^\circ$) of the substrate peak. This could be due to a partial relaxation of the sample. Optically, no cross hatching was observed for this normal MQW. Periodicity calculations for this sample yield periods of approximately 150Å. This indicates that the wells for this normal SLS are around 115Å and are balanced by 27Å wells with the remainder being comprised of two GaAs layers that are deposited in the interfaces of the wells and barriers. These values agree very well with the zero-stress calculations indicating great control over the growth of the MQW. Fig. 6-5(b) is a moderately staggered (1.5:1) MQW. The FWHM of these peaks are the narrowest of the three displayed and optically the surface was very clean with no cross hatching indicating that the structure was completely strained. Periodicity calculations of this structure yield a period thickness of approximately 300Å. This is twice that found for Fig. 6-5(a) which is to be expected as any staggering ratio effectively doubles the period. This periodicity gives well thicknesses of 138Å and 92Å and a barrier thickness of 27Å with the remainder being GaAs transition layers. Fig. 6-5(c) is the XRD data for a heavily staggered (5.667:1) MQW. Optically this sample displayed some cross hatching and this is reflected in the FWHM of the satellite peaks. The cross hatch was not systemic however. This non-systemic cross hatching indicates that it may be possible to stagger MQW structures to a ratio of 5.667:1 while maintaining pseudomorphic growth conditions. Periodicity calculations give a period thickness of 280Å with well thicknesses 176Å and 31Å and barrier thickness of 25Å. The change of period thickness is also indicative of relaxation.
Device p-i-n structures were grown utilizing both conventional and staggered MQW structures as the i-layer to evaluate their effect on device parameters. Staggering ratios of 3:1 (x=50) and 5.667:1 (x=70) were utilized for this analysis. It was determined from the spectral response, as seen in Fig. 6-6, that an improved extension was obtained from the higher staggering ratios. Both XRD and optical microscopy showed that the staggered MQW structures are strained with no relaxation occurring. Additionally, the fairly high EQE (without AR coating) seen in Fig. 5-6 indicates that carrier transport by means of tunneling occurs with close to 100% efficiency. IV measurements were also performed. Fill factors of 81.2% and 79.9% were obtained from these IV measurements for both the staggering ratio of 3:1 and 5.667:1, respectively. Additionally, $V_{oc}$ of 0.97V and 0.95V were obtained for the staggering ratios of 3:1 and 5.667:1, respectively. When comparing these results to that obtained from the standard GaAs cell, fill factor of 81.4% and $V_{oc}$ of 0.97, they indicate that these staggered MQW structures could offer an increase of about 0.7mA/cm$^2$ in current with a minor reduction of fill factor and $V_{oc}$.

To investigate how staggering overcame QSE, a model was developed and is presented in Fig. 6-7. From this model we determined that QSEs were reduced as the staggering ratio of 1:1 for our normal SLS was increased to 3:1. It should be noted that the x axis value of average well width is the average of both the thick and thin InGaAs wells. This is used to provide a normalized value making it easier to compare a normal SLS and any permutations of staggering thereof. The model was compared to experimental results to see how well it matched up to the observed extension past the GaAs band edge. These results have been labeled on Fig. 6-7 and agree very well with the model.

6.5 Conclusion

High phosphorus composition GaAsP (>75% P) was successfully grown by utilizing a saturation point on a calibration curve. This high composition of GaAsP was grown in conjunction with InGaAs in a strained layer superlattice structure where tunneling was the transport mechanism used to collect the minority carriers. Tunneling was only made possible by utilizing very thin barriers (~30 Å). While using thin, high composition GaAsP barriers is
advantageous when it comes to carrier transport and increasing the usable percentage of the MQW (the InGaAs wells make up a larger % of the MQW for structures utilizing tunneling as opposed to thermionic emission for carrier transport), they do impart some deleterious QSE into the InGaAs wells. It was shown that these QSE could be overcome by using a staggered MQW. We have shown that staggered MQWs result in further extension of the absorption edge when compared to the conventional MQW by minimizing the QSE. Also, the staggered MQW shows very good EQE, indicating that tunneling is an efficient carrier transport. These advantages occur with little reduction in both $V_{oc}$ and fill factor.

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Figure 6-1: General structure of the MQW demonstrating tunneling through thin (30Å), high composition GaAsP barriers (GaP%>70%).

Figure 6-2: Staggering of a standard MQW is achieved by moving the portion of on well to an adjacent well. A value of x=50 would result in a staggering ratio (thick well:thin well) of 3:1.
Figure 6-3: Phosphorus calibration with TBAs flow rate of 20 sccm, TMGa flow rate of 2 sccm and substrate temperature of 600°C.
Figure 6-4: Zero-Stress balance for GaAs$_{0.2}$P$_{0.8}$ barriers. The horizontal line represents the optimum barrier thickness that balances minority carrier transport and QSEs.
Figure 6-5: (004) XRD data for In$_{0.15}$Ga$_{0.85}$As/GaAs$_{0.2}$P$_{0.8}$ normal MQW (a), 1.5:1 Stagger MQW (b) and 5.667:1 Stagger MQW (c).
Figure 6-6: External quantum efficiency for a standard GaAs cell and two staggered p-i-n cells with staggering ratios of 3:1 and 5.667:1. Extension of the band edge is observed the larger a MQW is staggered. (Device fabrication provided by Geoffrey K. Bradshaw)
Figure 6-7: Staggered band gap model showing how staggering affects the band edge of the MQW. (Modeling provided by C. Zachary Carlin)
CHAPTER 7: Interface properties of Ga(As,P)/(In,Ga)As Strained Multiple Quantum Well Structures

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7.1 Abstract

(In,Ga)As/Ga(As,P) multiple quantum wells (MQWs) with GaAs interface layers have been characterized with photoluminescence (PL) and high resolution scanning transmission electron microscopy (STEM). By growing (In,Ga)As/Ga(As,P) MQWs with asymmetric GaAs interfacial layers, we found that phosphorus carry-over had a profound effect on the absorption edge of the (In,Ga)As wells. Evidence for this phosphorus was initially determined via PL and then definitively proven through STEM and energy dispersive x-ray spectroscopy. We show that the phosphorus carry-over can be prevented with sufficiently thick GaAs transition layers. Preliminary results for GaAs p-i-n solar cells utilizing the improved MQWs are presented.

7.2 Introduction

The MOCVD growth of multiple quantum well or superlattice structures by switching column III compounds, such as in GaAs/(In,Ga)As, result in fairly abrupt interfaces at the atomic level. However, when the switching involves column V compounds, such as at InGaP/GaAs or (In,Ga)As/Ga(As,P) interfaces, grown under high V/III ratio, achieving abrupt interface has been problematic. These column V switches are typically accompanied by the formation of quaternary alloys such as (In,Ga)AsP. This difficulty arises due to phosphorus and arsenic atoms intermixing as well as phosphorus carry-over. Phosphorus
carry-over and arsenic-phosphorus exchange have been extensively studied, with the most research being conducted on the InGaP/GaAs interfaces utilized in many optoelectronic devices.\textsuperscript{1,2} However, while some attempts have been made to mitigate these issues, there is still some debate upon the dominant mechanism governing the interface formation.

The focus of this study is to address the difficult formation of abrupt (In,Ga)As/Ga(As,P) hetero interfaces, particularly when utilizing high phosphorus, GaAs\textsubscript{0.2}P\textsubscript{0.8} barriers,\textsuperscript{3} and the unintentional creation of (In,Ga)AsP interfacial layers that interlope on (In,Ga)As wells when switching column V compounds. The predominant method used to improve MQW interface quality is a growth pause-purge switching sequence.\textsuperscript{4-6} Development of such method has not yet been successful with the precursors used in this study. An alternative way to improve (In,Ga)As/Ga(As,P) interface quality is through the utilization of GaAs transition layers. In this study, an absorption edge discrepancy was investigated utilizing asymmetric GaAs interfacial transitions for our (In,Ga)As/Ga(As,P) MQW. We show that through the use of GaAs transitions it is possible to prevent phosphorus carry-over between the barrier and well structures. Additionally, the interface layers at the two interfaces, phosphorus to indium and indium to phosphorus, were investigated with respect to their structural, electrical and optical properties utilizing room temperature photoluminescence (PL), high resolution scanning transmission electron microscopy (STEM) and spectral response of p-i-n cells with MQW structures.

The motivation of developing this MQW is to improve the current matching conditions in the (In,Ga)P/GaAs/Ge multijunction (MJ) cell while maintaining lattice matched conditions. The MQW will be part of the middle GaAs cell to extend the absorption to a longer wavelength. The workhorse of the MQW structure is the (In,Ga)As well, which is grown pseudomorphically and under compressive strain with respect to the GaAs substrate. Barriers composed of Ga(As,P) are utilized to balance the strain introduced into the structure by the (In,Ga)As wells; as such, these barriers are under tensile strain. A schematic representation of and more growth detail can be found in our previous work.\textsuperscript{3} This MQW has been used for LEDs,\textsuperscript{7} solar cells\textsuperscript{8} and means for defect reduction in heteroepitaxy.\textsuperscript{9}
The metalorganic chemical vapor deposition (MOCVD) epitaxial growth of the (In,Ga)As/Ga(As,P) MQW structures was performed on (100) substrates oriented 2° towards the (110) at 200 torr. Trimethlygallium (TMGa), trimethylindium (TMIn) and trimethylaluminum (TMAl) were used as group-III sources while tert-butylarsine (TBAs) and tert-butylphosphine (TBP) were used as group-V sources. Substrate temperature during growth was kept constant at 575°C for all MQW. We found during previous investigations that placing thin GaAs layer (7Å) at the MQW interfaces improved both electrical and material characteristics. This structure will be denoted as the standard MQW structures during the following discussions.

7.4 Results and Discussion

The standard MQW structures were investigated by photoluminescence with constant (In,Ga)As compositions of 16% indium but variable well thicknesses ranging from 77 to 144 Å. Barrier compositions and thicknesses of 80% phosphorus and 30 Å, respectively, were constant for this initial set of samples. This resulted in non-strain balanced samples, however all samples were grown sufficiently thin to prevent relaxation through strain buildup and was confirmed through both optical microscopy and x-ray diffraction. The PL data was then graphed against the inverse of the squared well thickness (1/L^2), as the energy levels within the well vary proportionally with this parameter, Fig. 7-1. For convenience, data points include the well thickness. The dashed line in Fig. 7-1 shows the least-squares regression for the MQWs with the three widest (In,Ga)As wells.

For the thickest wells, the measured peak PL values correspond well to the theoretical values. However, the PL measurements for the thin wells deviated greatly from the expected values, indicating that something was affecting the thinner wells. It is important to remember that, while thicker wells behaved as predicted, the wells must remain thin enough to be strain balanced with 30Å Ga(As,P) barriers when incorporated into a device. Three possible sources for the discrepancy between experimental and predicted results were considered. The first is that the indium turn-on was slow and resulted in the production of wells which suffer greatly from quantum size effects (QSE), thus raising the emission of the wells as seen in
Fig. 7-1. The second possible source is a turn-off delay, or carry-over, of phosphorus into the wells. This would result in a quaternary alloy with a much higher band gap than the intended (In,Ga)As. The third is an arsenic-phosphorus exchange. However, this exchange would be expected to only occur for a couple of monolayers of growth and while it would cause some deviation in MQW emission, it would not account for the large deviation observed.

To investigate whether the MQW emission discrepancy was due to slow indium turn-on or phosphorus carry-over, a series of three, 20 period MQW samples were produced where the wells and barriers were kept constant while the GaAs transition layers were varied. These samples were composed of In$_{0.2}$Ga$_{0.8}$As/GaAs$_{0.2}$P$_{0.8}$ with thicknesses of 94Å and 30 Å for the wells and barriers, respectively. A set of samples was investigated where only the GaAs transition layers were varied (7 Å to 70 Å). The generalized ideal conduction band diagrams for the three samples, in addition to the PL results, are presented in Fig. 7-2. It should be noted that the PL responses presented in Fig. 7-2 have all been normalized. The first sample (a) was produced with standard MQW GaAs intermediate layers of 7 Å. This sample gave a PL recombination wavelength of 970 nm. The second sample (b) contained GaAs transition layers of 70 Å at the Ga(As,P)$\rightarrow$(In,Ga)As transitions with respect to the growth direction, represented by Z in Fig. 7-2. Photoluminescence gave an emission wavelength of 1015 nm, a vast improvement over the standard MQW sample. This result is an indication that the root cause of the emission discrepancy in the MQW was occurring at the Ga(As,P)$\rightarrow$(In,Ga)As interface. To be sure, a third sample (c) was produced in which the GaAs transition layer at the (In,Ga)As$\rightarrow$Ga(As,P) interface was increased to 70 Å. This sample resulted in a PL response the same as the standard MQW sample, further confirming problems at the phosphorus to indium transition. If slow indium turn-on had been the predominate issue behind our emission discrepancy the three aforementioned samples would have had similar PL responses with respect to emission wavelength. Ultimately, this data suggests that there is a phosphorus carry-over from the barriers into the wells resulting in the observed emission discrepancy.

Samples for electron microscopy were prepared by wedge polishing followed by Ar$^+$ ion milling with a Fischione (Export, PA) model 1050. A probe corrected FEI Titan G2 60–
300 kV S/TEM equipped with an X-FEG source and an advanced Super-X™ EDS detector system operated at 200 kV was used for high angle annular dark field (HAADF) STEM and EDS mapping. The convergence semi-angle was 21 mrad. The Bruker ESPRIT software package was used for drift correction during acquisition and post-processing with a 3-pixel smoothing filter to reduce noise. Electron microscopy was performed on the two samples presented in Fig. 7-2 with 70 Å GaAs transition layers. Fig. 7-3a shows HAADF STEM of the 70 Å GaAs transition layers at the Ga(As,P)→(In,Ga)As interface. Well-defined interfaces were observed throughout the sample. The (In,Ga)As→Ga(As,P) interface sample with the 70 Å GaAs transition layers is shown in Fig. 7-3b, and demonstrates qualitatively similar interfaces to the Ga(As,P)→(In,Ga)As sample. Further analysis of the Ga(As,P)→(In,Ga)As atomic distribution required chemical analysis by EDS. The EDS maps presented in Fig. 7-3 demonstrate that phosphorus carries over into the subsequent growth. It should be noted that the indium also shows a slight carry-over effect. However, this only affects the strain balance of the MQW and has minimal effect on the MQW Ga(As,P) barrier band gap with 80% GaP. Line scans were generated utilizing the EDS maps of the two samples and are presented in Fig. 7-4. Growth direction is from left to right for both images. The line scans show that strong phosphorus carryover occurs when In$_{0.23}$Ga$_{0.77}$As was grown directly after Ga(As,P) without the thick GaAs transition. From these line scans it was determined that the phosphorus carry-over occurs for ~30 Å.

In a standard MQW, one containing 7Å GaAs transitions, the phosphorus carry-over blends through the narrow GaAs transition and into part of the (In,Ga)As wells. This results in a quaternary alloy with a higher band gap, effectively narrowing the wells. However, when utilizing sufficiently thick GaAs, the phosphorus carry-over can be confined strictly to the GaAs transition layer.

The interest in this research arises from the desire to optimize the performance of the GaAs middle cell in the MJ solar cell structures by improving current matching conditions. The MQW was inserted in the i-layer of a p-GaAs/i-MQW/n-GaAs device to extend the absorption edge beyond that of the GaAs while maintaining the lattice matching conditions. The total thickness of the MQW structure is of importance to device performance; it should
be thick enough to enhance optical absorption while not exceeding the depletion region. It is desirable that most of the depletion layer be made of the current generating (In,Ga)As wells. Therefore, it would be most beneficial to grow the GaAs transition layer at the \( \text{Ga(As,P)→(In,Ga)As} \) interface only as thick as necessary to prevent phosphorus carry-over into the well. This optimized configuration would result in the most efficient MQW in terms of space utilization. Two devices were prepared utilizing thicker GaAs transitions of 15 Å and 22 Å at the \( \text{Ga(As,P)→(In,Ga)As} \) interfaces. These MQW structures were 10 periods. Spectral response for these devices, in addition to a standard non-MQW GaAs cell, is presented in Fig. 7-5. The spectral response results are in reasonable agreement with the PL data, where peak emission for the 15Å and 22Å GaAs intermediate layers is 940nm and 960nm respectively, results not shown. These results show the expected extension of the GaAs device absorption edge due to the GaAs MQW transition layers. Nevertheless, the optimum thickness for the GaAs transition layer must be determined to properly balance the reduction of phosphorus carry-over into the well, and subsequent absorption edge extension, without compromising the total number of (In,Ga)As wells which can be grown in a given depletion thickness. Future research is aimed at answering these questions.

7.5 Conclusion

In conclusion, we have studied the interfacial properties of the high phosphorus Ga(As,P)/(In,Ga)As MQW interfaces. We have found switching indium off at the termination of the wells, while switching phosphorus on at the onset of the barriers, to be fairly abrupt. Additionally, we found that switching indium on at the onset of well growth was abrupt. However, phosphorus switching off at the termination of the barriers was not abrupt and resulted in phosphorus carry-over in the subsequent (In,Ga)As growth. From PL studies the presence of phosphorus in the well resulted in a blue shift in the emission of the (In,Ga)As well. This deleterious carry-over was reduced by the introduction of a thick GaAs transition layer at the \( \text{Ga(As,P)→(In,Ga)As} \) interface. This thick GaAs transition layer resulted in a red shift (extension of the observed PL emission to longer wavelengths) in the (In,Ga)As wells and was observed via PL. HAADF STEM and EDS studies show that the
phosphorus carry-over extends ∼30 Å into the GaAs intermediate layer. These results will extend the absorption edge of GaAs solar cells utilizing MQW within the depletion region to longer wavelengths, resulting in more efficient cells.

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Figure 7-1: (a) The PL data for a series of In$_{0.18}$Ga$_{0.82}$As/GaAs$_{0.2}$P$_{0.8}$, 20 period MQW samples with varying (In,Ga)As well thickness, L. (b) The peak PL emission graphed vs. 1/L$^2$. (Modeling provide by C. Zachary Carlin)
Figure 7-2: PL data for three In$_{0.23}$Ga$_{0.77}$As/GaAs$_{0.2}$P$_{0.8}$, 20 period MQW samples with constant well and barrier thickness but variable GaAs transitions of: (a) 7Å at both MQW interface transitions, (b) 70Å at the Ga(As,P) to (In,Ga)As transition but 7Å at the (In,Ga)As to Ga(As,P) transition and (c) 7Å at the Ga(As,P) to (In,Ga)As transition but 70Å at the (In,Ga)As to Ga(As,P) transition.
Figure 7-3: HAADF STEM images and EDS plots for two In$_{0.23}$Ga$_{0.77}$As/GaAs$_{0.2}$P$_{0.8}$, 20 period MQW structures with GaAs transitions of: (a) 70Å at the Ga(As,P) to (In,Ga)As transition but 7Å at the (In,Ga)As to Ga(As,P) transition and (b) 7Å at the Ga(As,P) to (In,Ga)As transition but 70Å at the (In,Ga)As to Ga(As,P) transition. (STEM provided by James M. LeBeau and Hamideh M. Alipour)

Figure 7-4: EDS line scans of two In$_{0.23}$Ga$_{0.77}$As/GaAs$_{0.2}$P$_{0.8}$, 20 period MQW structures with GaAs transitions of: (a) 70Å at the Ga(As,P) to (In,Ga)As transition but 7Å at the (In,Ga)As to Ga(As,P) transition and (b) 7Å at the Ga(As,P) to (In,Ga)As transition but 70Å at the (In,Ga)As to Ga(As,P) transition. (STEM provided by James M. LeBeau and Hamideh M. Alipour)
Figure 7-5: External quantum efficiency for two GaAs-In$_{0.23}$Ga$_{0.77}$As/GaAs$_{0.29}$P$_{0.71}$ MQW, 10 period devices with MQW GaAs transitions of (a) 15Å at the Ga(As,P) to (In,Ga)As transition but 7Å at the (In,Ga)As to Ga(As,P) transition and (b) 22Å at the Ga(As,P) to (In,Ga)As transition but 7Å at the (In,Ga)As to Ga(As,P) transition. (Device fabrication provided by Geoffrey K. Bradshaw)
CHAPTER 8: Effect of GaAs interfacial layer on the performance of high bandgap tunnel junctions for multijunction solar cells

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8.1 Abstract

The effect of the heterojunction interface on the performance of high bandgap In₀.₃Ga₁₋₀.₃P:Te/Al₀.₆Ga₀.₄As:C tunnel junctions was investigated. The insertion of 30Å of GaAs:Te at the junction interface resulted in a peak current of 1000A/cm² and a voltage drop of ~3mV for 30A/cm² (2000× concentration). The presence of this GaAs interfacial layer also improved the uniformity across the wafer. This architecture could be used within multijunction solar cells to extend the range of usable solar concentration with minimal voltage drop.

8.2 Introduction

Concentrator photovoltaics (CPV) have generated considerable interest as a means of achieving high efficiency, potentially reducing the levelized cost of PV generated energy. Both open-circuit voltage and short-circuit current increase under increasing solar concentration. However, the fill factor (FF) decreases at very high solar concentrations, leading to a reduction in efficiency. The deleterious reduction in FF is caused by an increase in voltage drop across the sheet and contact resistance (R_C) in addition to the voltage drop across the tunnel junction (TJ). For solar concentrations above 1000×, there are several requirements for optimal TJ operation. First, series resistance must be minimized for a low voltage drop; this requires, at the very least, the TJ must have a peak current density (J_p)
higher than that generated by the cells at high solar concentration. Second, for optimum efficiency the TJ must consist of materials with bandgaps at least as high as the active subcell material above it. Third, the dopants used for highly doped layers of the TJ should have very low diffusion coefficients to prevent deterioration of the junction during subsequent growth steps.

The AlGaAs:C/InGaP:(Se or Te) ternary/ternary (T/T) TJ structure for the GaAs/InGaP based multijunction solar cell (MJSC) was first reported in the 1990s. The voltage drop across this TJ at a current density corresponding to a solar concentration of 2000× was approximately 40mV. For triple junction MJSC structures, the voltage drop across two TJs will be approximately 100mV. This voltage drop results in a MJSC efficiency reduction of approximately 4% and is a target for further improvements.

The quality of the TJ depends critically on the metallurgical interface quality. For T/T TJs grown by metalorganic chemical vapor deposition (MOCVD), there are several issues that must be addressed to achieve both abrupt compositional and doping transitions at the interface. Because a substantial overpressure of group V precursors is required during growth, compositional abruptness is fairly difficult to achieve in MOCVD when column V precursors need to be switched on and off. For example, it has been recently demonstrated through STEM energy dispersive spectroscopy, that switching In off in an InGaAs/GaAsP multiple quantum well (MQW) structure is fairly abrupt, while switching P off is not. This results in P carry-over into the subsequent growth for approximately 30Å. Thus, it is expected for an abrupt In₀.₀₅Ga₀.₉₅P:Te/Al₀.₆Ga₀.₄As:C TJ that P will be present in the Al₀.₆Ga₀.₄As:C, resulting in a graded alloy composition at the tunnel junction interface. In addition to P carry-over, the termination of the Te doping for the In₀.₀₅Ga₀.₉₅P:Te at the onset of the Al₀.₆Ga₀.₄As:C growth is not abrupt due to the memory effect, or surface segregation, of Te, as well as its solubility limit in InGaP. Thus, grading of both alloy composition and doping are expected in T/T tunnel junctions. This leads to variations in the depletion and tunneling thickness for carriers and will impact both the peak tunneling current (Jₚ) and the TJ Rₛ. TJ characteristics across wafers and from wafer-to-wafer show spreads that would affect solar cell efficiencies. Other researchers have resorted to using the
GaAs:n^{++}/AlGaAs:p^{++} binary/ternary (B/T) TJ\textsuperscript{5,6} where problems such as column V switching are avoided, yielding better reliability and reproducibility; however, this B/T TJ suffers from the absorption of photons by the low bandgap GaAs:n^{++} layer that reduces the efficiency of the MJSC.\textsuperscript{7,8}

This paper addresses the interface properties of T/T TJs. The effect of an interfacial GaAs layer, which forms a ternary/binary/ternary (T/B/T) structure as shown in Fig. 8-1, on peak current and voltage drop across the junction have been investigated. We show methods to achieve a very high, more reproducible peak TJ current with properties suitable for solar applications with concentration ≥2000×. Recently it has been reported that the addition of a MQW structure at the interface of a TJ lattice matched to InP resulted in the enhancement of $J_p$. However, it is also accompanied by a 1.7% absorption of the photons in the spectral band of interest.\textsuperscript{9}

8.3 Experimental

The TJ structures were grown using a Thomas Swan metalorganic chemical vapor deposition (MOCVD) system with a custom built, vertical reaction chamber. (100) GaAs:Si 2°→(110) substrates were utilized for all growth. Metalorganic precursors employed included: trimethylgallium (TMGa), trimethylindium, trimethylaluminum, tert-butylarsine, tert-butylphosphine (TBP), carbon tetrabromide (CBr$_4$), diethyltelluride (DETe) and dimethylzinc. The growth temperature for the In$_x$Ga$_{1-x}$P:Te/Al$_{0.6}$Ga$_{0.4}$As:C TJ was chosen to produce both high quality material and adequate doping levels for both sides of the junction. Utilizing CBr$_4$, we found that the Al$_{0.6}$Ga$_{0.4}$As:C doping decreased with an increase in growth temperature. The growth optimization for the Al$_{0.6}$Ga$_{0.4}$As:C was achieved at 580°C, resulting in a hole doping concentration of 8×10$^{19}$ cm$^{-3}$. The growth of nearly lattice matched In$_x$Ga$_{1-x}$P:Te, slightly compressive with respect to GaAs, was optimized at 580°C. Doping levels of approximately 1.15×10$^{19}$ cm$^{-3}$ were achieved, which is believed to be the saturation limit for Te incorporation in InGaP.\textsuperscript{4} Interfacial layers of GaAs:Te grown at the same DETe and TMGa flow rates produced doping levels of 2×10$^{19}$ cm$^{-3}$. 

The TJ's were capped with 2200Å of GaAs:Zn utilizing doping levels of \( \sim 3 \times 10^{19} \text{ cm}^{-3} \) to achieve ohmic contacts with low \( R_C \). The composition of the In\(_x\)Ga\(_{1-x}\)P:Te was adjusted such that the tensile stress in Al\(_{0.6}\)Ga\(_{0.4}\)As:C, due to the carbon doping, was compensated by the compressive stress of the In\(_x\)Ga\(_{1-x}\)P:Te to achieve an overall slightly compressive TJ pseudomorphic to the GaAs substrate as demonstrated by the XRD image presented in Fig. 8-2. For convenience, the XRD peaks have been labeled with the layers responsible for them. The thicknesses of the In\(_x\)Ga\(_{1-x}\)P:Te and Al\(_{0.6}\)Ga\(_{0.4}\)As:C layers were 1800Å and 1200Å, respectively, as determined by scanning electron microscopy.

Devices were processed into 0.09mm\(^2\) mesas using standard lithography processes. Prior to metallization, the mesas were adequately etched using the following sequence. After a 30s HCl dip, the GaAs cap and AlGaAs layers were removed using 3:1:50 H\(_3\)PO\(_4\):H\(_2\)O\(_2\):H\(_2\)O etch with GaInP acting as an etch stop. HCl (30% by vol.) was used to etch InGaP and finally a 1:1:3 H\(_3\)PO\(_4\):H\(_2\)O\(_2\):H\(_2\)O etch was used to etch slightly below the growth. The p-type contacts used consisted of Ti/Pd/Ag/Au annealed at 450°C for 60s and n-type contacts of Pd/Ge/Ti/Pt/Ag/Au annealed at 300°C for 15s. The specific contact resistances, measured using transmission line method, for these metallization schemes were \( 5 \times 10^{-7} \text{ Ω-cm}^2 \) and \( 2 \times 10^{-6} \text{ Ω-cm}^2 \) for the p- and n-type contacts, respectively.

### 8.4 Results and Discussion

We studied the effect of a GaAs:Te interfacial layer at the metallurgical junction of the TJ. Fig. 8-3 shows the J-V characteristics of (a) an abrupt T/T TJ structure and (b) a T/B/T TJ architecture with a 30Å GaAs:Te interfacial layer. The \( J_p \) obtained strongly depends on the thickness of the GaAs intermediate layer and ranges from 12 A/cm\(^2\) for the direct interface to over 1000 A/cm\(^2\) for the thicker GaAs interfacial layer TJ's. These results indicate that an abrupt T/T structure is barely suitable for solar concentrations of 1000x whereas the T/B/T structure with a 30Å GaAs:Te interfacial layer can accommodate solar concentrations as high as 70000x, with negligible optical absorption in the 30Å GaAs:Te interfacial layer.

The range of peak current (\( J_p \)) obtained from three different T/B/T TJ's, in addition to the standard T/T TJ, is presented in Fig. 8-4. The spread of the data shown in Fig. 8-4 is due
to spatial variation in the $J_p$ across the wafer. For the direct T/T architecture, $J_p$ varies by a factor of three while $J_p$ of the T/B/T structures with 30Å GaAs:Te interfacial layers varies by less than a factor two. The primary conclusion of Fig. 8-4 is the vast improvement of the TJ $J_p$ due to the GaAs:Te interfacial layer.

The achievement of a TJ with $J_p$ of $\sim 1000\, \text{A/cm}^2 (\sim 70000 \times)$ should be viewed purely as an academic achievement. It is not expected that a MJSC will ever operate at such large solar concentrations due to practical limitations such as heat dissipation issues. The practical impact of the current work is to demonstrate that a high bandgap TJ with a thin GaAs:Te intermediate layer will reproducibly achieve a low voltage drop at more reasonable 30A/cm$^2$ (2000× solar concentration). The addition of 30Å and 45Å GaAs:Te interfacial layers results in a voltage drop in the range of 2.5 to 6mV, respectively, as shown in Fig. 8-5(a) and 8-5(b). Additionally, the spread in the voltage drop across a given sample for both the 30Å and 45Å GaAs:Te interfacial layers is very narrow, on the order of a few mV. Thus, the insertion of the GaAs:Te interfacial layer can allow the MJSC to achieve more reproducible results with variation in efficiency less than 0.2%, while retaining the efficiency gains ($\sim 1\%$ absolute) due to the increased transparency of the T/T TJ compared to the B/T TJ. Results shown in Fig. 8-3a, Fig. 8-5a and Fig. 8-5b are superior to the best reported data for high bandgap TJs. For example, Spectrolab reported $J_p$ of 637A/cm$^2$ with a voltage drop of 400mV across the junction.$^{10}$

8.5 Conclusion

We studied the impact of GaAs:Te interfacial layers on high bandgap InGaP:n$^{++}$/AlGaAs:p$^{++}$ TJ peak current and voltage drop at current densities associated with high solar concentration ($\times \geq 2000$). MOCVD-grown abrupt T/T tunnel junctions are barely suitable for 2000×, 30A/cm$^2$ applications and values of $J_p$ vary across and between wafers. Uniformity and $J_p$ are improved when the T/T is replaced by a T/B/T structure. The addition of a GaAs:n$^{++}$ layer with a thickness of about 30Å achieved a $J_p$ of 1000A/cm$^2$ with only a $\sim 3$ mV voltage drop across the junction at 30A/cm$^2$. This improvement can be explained by the lower electron effective mass and higher doping in the GaAs. The high tunneling current
achieved in these TJ with a voltage drop of only a few mV across the junction can allow MJ solar cells to operate at higher concentrations with little deterioration in fill factor for concentrations up to 2000 suns while retaining the high current provided by the low absorption high bandgap TJ.

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Figure 8-1: Schematic of the InGa1-xP:Te/Al0.6Ga0.4As:C tunnel junction.
Figure 8-2: Typical In$_{x}$Ga$_{1-x}$P:Te/Al$_{0.6}$Ga$_{0.4}$As:C tunnel junction XRD showing the compressive and tensile strain of the In$_{x}$Ga$_{1-x}$P:Te and Al$_{0.6}$Ga$_{0.4}$As:C layers, respectively. (XRD done in collaboration with Jeffrey L. Harmon)
Figure 8-3: J-V for (a) $\text{In}_x\text{Ga}_{1-x}\text{P:Te/Al}_{0.6}\text{Ga}_{0.4}\text{As:C}$ T/T tunnel junction and (b) $\text{In}_x\text{Ga}_{1-x}\text{P:Te/GaAs:Te/Al}_{0.6}\text{Ga}_{0.4}\text{As:C}$ T/B/T tunnel junction utilizing a 30Å GaAs:Te interfacial layer. (Device fabrication provided by Geoffrey K. Bradshaw)
Figure 8-4: Peak tunneling current range for various In$_x$Ga$_{1-x}$P:Te/GaAs:Te/Al$_{0.6}$Ga$_{0.4}$As:C tunnel junction architectures with GaAs:Te interfacial layer thickness ranging from 0Å to 45Å. (Device fabrication provided by Geoffrey K. Bradshaw)
Figure 8-5: Voltage drop across the T/B/T TJs at a solar concentration of 2000× for (a) 30Å GaAs:Te interfacial layers and (b) 45Å GaAs:Te interfacial layers. (Device fabrication provided by Geoffrey K. Bradshaw)
CHAPTER 9: Conclusion

9.1 Conclusion

Strain/Stress-balanced Multi-quantum well structures comprised of InGaAs/GaAsP show a high degree of promise for extending the absorption edge of GaAs photovoltaic cells and InGaP/(In)GaAs/Ge multijunction photovoltaics. High phosphorus composition GaAsP (>75% P) barriers were successfully grown by utilizing a saturation point on a calibration curve. This high composition of GaAsP was grown in conjunction with InGaAs in a strain/stress-balanced MQW structure where tunneling was the transport mechanism used to collect the minority carriers. Tunneling was only made possible by utilizing very thin barriers (~30 Å). While using thin, high composition GaAsP barriers is advantageous when it comes to carrier transport and increasing the usable percentage of the MQW (the InGaAs wells make up a larger % of the MQW for structures utilizing tunneling as opposed to thermionic emission for carrier transport), they do impart some deleterious QSE into the InGaAs wells. It was shown that these QSE could be overcome by using a staggered MQW. We have shown that staggered MQWs result in further extension of the absorption edge when compared to the conventional MQW by minimizing the QSE. Also, the staggered MQW shows very good EQE, indicating that tunneling is an efficient carrier transport. These advantages occur with little reduction in both Voc and fill factor.

The effect of thicker GaAs transition layers at the interfaces within the MQW structure was investigated. It was found that switching indium off at the termination of the wells, while switching phosphorus on at the onset of the barriers, was fairly abrupt. Additionally, it was found that switching indium on at the onset of well growth was abrupt. However, phosphorus switching off at the termination of the barriers was not abrupt and resulted in phosphorus carry-over in the subsequent InGaAs growth. From PL studies the presence of phosphorus in the well resulted in a blue shift in the emission of the InGaAs well. This deleterious carry-over was reduced by the introduction of a thick GaAs transition layer at the GaAsP→InGaAs interface. This thick GaAs transition layer resulted in a red shift (extension of the observed PL emission to longer wavelengths) in the InGaAs wells and was observed via PL. HAADF STEM and EDS studies show that the phosphorus carry-over
extends ~30 Å into the GaAs intermediate layer. These results will extend the absorption edge of GaAs solar cells utilizing MQW within the depletion region to longer wavelengths, resulting in more efficient cells. The utilization of thicker GaAs transition must be investigated with the staggered MQW architecture to determine their compatibility with one another. It is hoped that these GaAs transition layers will red shift the narrow staggered well absorption edge to useable wavelengths beyond that of the GaAs cell.

With the knowledge gained from the MQW development, the impact of GaAs:Te interfacial layers on high bandgap InGaP:n++/AlGaAs:p++ TJ peak current and voltage drop at current densities associated with high solar concentration (×≥2000) was investigated. Current generation, MOCVD-grown abrupt T/T tunnel junctions are barely suitable for applications at high solar concentration (≥2000×, ≥30A/cm). Uniformity and Jp are improved when the T/T is replaced by a T/B/T structure. The addition of a GaAs:n++ layer with a thickness of about 30Å achieved a Jp of 1050A/cm2 with only a ~3 mV voltage drop across the junction at 30A/cm2. This improvement can be explained by the lower electron effective mass and higher doping in the GaAs. The high tunneling current achieved in these TJ with a voltage drop of only a few mV across the junction can allow MJ solar cells to operate at higher concentrations with little deterioration in fill factor for concentrations up to 2000 suns while retaining the high current provided by the low absorption high bandgap TJ. Further development and optimization of the T/B/T TJ must continue.

It is hoped that the work presented herein will help terrestrial solar power generation to gain a much larger foothold in the energy generation sector. Ultimately, this will result in a world less dependent on fossil fuels.
References

Chapter 1


8. “How Much Natural Gas does the United States have and how long will it last?” *U.S. Energy Information Administration, DOE/EIA*, 29 August 2012, Web: http://www.eia.gov/tools/faqs/faq.cfm?id=58&t=8


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1. Razeghi, M., et al. "Ga0. 51In0. 49P/GaxIn1-xAs lattice-matched (x= 1) and strained (x= 0.85) two-dimensional electron gas field-effect transistors." *Semiconductor science and technology* 6.2 (1991): 103.


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