III-V DILUTE NITRIDE MULTI-QUANTUM WELL SOLAR
CELLS FOR HIGH EFFICIENCY PHOTOVOLTAICS

A Dissertation Presented to
the Faculty of the Department of Physics
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
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III-V DILUTE NITRIDE MULTI-QUANTUM WELL SOLAR CELLs FOR HIGH EFFICIENCY PHOTOVOLTAICS

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Abstract

Addition of a few percent of nitrogen to conventional III-V semiconductor alloys creates a surprising reduction of the host band-gap. Due to their unusual band-gap characteristics, dilute nitride III-V semiconductor alloys such as Ga(In)AsN are suitable candidates to serve as a 1eV 3\textsuperscript{rd} junction sub-cell in current high efficiency multi-junction solar cells, and are projected to achieve solar cell efficiencies of ~40%. In order to overcome material constraints such as poor minority carrier lifetime and doping issues in dilute nitrides, prior work has involved insertion of quantum well (QW) nanostructures of dilute nitrides within the intrinsic region of a solar cell, nevertheless, issues of carrier extraction have persisted. In order to improve upon this design, in this work, the band structure and energy levels of dilute nitride multi-quantum-well (MQW) system are calculated, from which the absorption coefficient is evaluated as a function of strain, nitrogen concentration, and electric field strength. Fitting the simulated value of absorption to experimental results showed incomplete extraction of carriers in the multi-quantum well region. Experimental characterization of previously grown dilute nitrides revealed the presence of a parasitic nitridation of the GaAsN/GaAs interface. Improvement of QW quality was done by using a modified run-vent system reduced nitridation. Improvement of carrier extraction was proposed based on the calculations of thermally assisted resonant tunneling QW design, and preliminary devices were grown to test this design. Results included a record open circuit voltage of 636 mV, and improved carrier extraction from resonant tunneling MQW solar cells of ~1eV, enabling future fabrication of multi-junction devices with efficiencies of ~39% (1 sun) and ~49% (500 sun conc).
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Chapter 1: Introduction

Since the turn of the 20\textsuperscript{th} century, the demand for energy has grown substantially with each passing decade, with a current demand of 15 TW-yr. Meeting this demand is one of the primary challenges for current technology. The prevalent use of non-renewable resources such as fossil fuels or nuclear material has raised concern due to their environmental impact and also health concerns. Hence, renewable sources of energy have seen an accelerated interest. In fact, numerous scenarios projected levels of renewable energy for 2020 that were already surpassed by 2010 [1].

Among renewable sources of energy, the primary source is the sun, which in addition to generating the necessary energy for wind, hydroelectricity and biomass, also provides up to 125000 TW of energy all over the earth. Among the several ways in which solar energy can be utilized (heat engines, photosynthesis, etc.), photovoltaics (PV) involves harvesting solar energy to produce electricity directly.

Among renewable sources of energy, solar PV is a fast-growing industry in the current decade. It took nearly four decades to install 50 GW of PV capacity worldwide. But in the last 3 years, the industry capacity has reached 140 GW, while global module prices have fallen 62 percent since 2011[1]. However, the primary challenge of PV is to reduce the overall cost per watt for the average consumer. Since cost of installation depends on
general economic and policy conditions, the key area for scientific improvement is the material and conversion efficiency of solar cells.

1.1 High Efficiency Solar cells

Solar cells are made with a variety of materials such as Si, Ge, CdTe, GaAs, InGaP, etc. They are generally referred to according to the corresponding period of the periodic table, e.g. III-V or II-VI materials. Traditionally, crystalline-silicon based solar cells have dominated the market, as silicon is abundant, cheap, non-toxic, and has a well established infrastructure in the semiconductor-electronics industry. They are referred to as 1st generation solar cells. 2nd generation solar cells utilize primarily “thin-film” materials, where the name refers to the comparison with crystalline Si, which has low absorption requiring thicker material for PV. Thin films cells made of CdTe, CuInGaSe₂ (CIGS), amorphous Si, etc. and have significantly reduced costs, yet exhibit poorer performance than crystalline Si solar cells. The 3rd generation of PV materials, which would be the focus of this work, involves among others, the use of multi-junction cells (tandem cells), or solar cells of different absorption ranges (band-gaps) that are stacked up in a series in order to absorb more of the incoming radiation, and hence deliver higher conversion efficiencies.
They have also been further improved by inclusion of quantum nanostructures, light-recycling mechanisms, surface texturing etc. [2]. As shown in Fig. 1.2, efficiencies of multi-junction systems have been highest in the whole range of photovoltaic materials.
Figure 1.2 Efficiency vs Time data showing high efficiencies achieved by multi-junction systems. [Data courtesy NREL, CO]

Multi-junction systems require lattice matching, where the lattice constants of the materials stacked serially match as well as possible, avoiding the formation of defects in the crystal during the manufacturing process. This narrows the set of options available to a specific set of alloys (see Fig. 1.3).
A good candidate for a 3-junction system has been the InGaP/GaAs/Ge system. Three to four junction devices incorporating 0.9-1.2 eV sub-cells are expected to pave the way to >50% conversion efficiencies. However, there was no available system lattice matched to GaAs available until the 1990’s, when dilute nitrides were investigated.

1.1.1 *Dilute Nitride Materials for Solar Cells*

Interestingly, the addition of a small percentage of nitrogen to III-V materials like GaAs reduces their band-gap drastically [3], i.e., it was possible to obtain a band-gap of 1eV material lattice matched to GaAs with GaInAsN, making it a perfectly suitable material for a 3rd junction in a 4-junction setup as was suggested by Hou et al., [4] (See Fig. 1.4).
Figure 1.4 Schematic from [4] showing an estimated efficiency of 42.3% under 1 sun AM0 (1350 Wm⁻²) for a 4J system using InGaAsN as the 3rd junction (1.02 eV)

Following this suggestion, numerous attempts had been made to fabricate this junction, but doping issues [5] and very short diffusion lengths of electrons in dilute nitrides [6], [7] prevented optimal functioning of these devices. A way to overcome this issue was to insert quantum wells of dilute nitrides within a GaAs sub-cell, which was pioneered at University of Houston [8] prior to the start of this work. Modifications and improvement to this design constitute the objective of this work.

1.1.2 Outline of the manuscript

This dissertation examines the possibility of obtaining high-efficiency solar cells using dilute nitride materials and quantum-nanostructure design. After this introductive chapter the manuscript is organized as follows.
In Chapter 2, a short history of the photovoltaic effect and the occasions where semiconductors were discovered and used for that purpose is presented since historically the experimental discoveries predated semiconductor theory. The principle of photovoltaic conversion is then described, by first clarifying the properties of sunlight. This is followed by a description of physics of semiconductors, including descriptions of band-gap, density of states and quantum confinement. Use of p-n junctions for photovoltaic conversion is then introduced, and major loss mechanisms in these devices are described. The final part of the chapter discusses various device designs for obtaining high conversion efficiency.

Chapter 3 focuses on theoretical modeling of a dilute nitride quantum well system, focused on light absorption. Following a description of the unique material properties of dilute nitrides, such as their anomalous band-gap shrinkage, high effective mass and diffusion lengths, a way to overcome these drawbacks by the use of quantum wells in dilute nitride solar cells is presented. A method based on the transfer-matrix formalism for predicting confined energy levels is described in detail. Energy transitions between hole and electron levels are presented and calculation of the electric field’s effect upon the absorption strength is shown. Finally, a motivation, in terms of a possible hindrance for carrier extraction, is provided for the necessity of accurate control over quantum well growth to enable the practical feasibility of the proposed multi-quantum well design.

In Chapter 4, the experimental procedures are elaborated. Use of molecular beam epitaxy and nitrogen plasma source for growth of dilute nitrides is described. Characterization of
samples grown earlier is described, showing the need to design a system with minimal nitrogen leakage into the chamber to prevent unwanted contamination and spikes in flux. A mechanical run-vent system then designed to circumvent the problem of nitrogen transients and flux control encountered in commercially available plasma sources. The effect, of using this design on the growth quality, both in-situ and after-growth, are evaluated and reveals a significant improvement in quantum well interface quality and optical properties of hetero-structures fabricated using this novel nitrogen delivery system.

Chapter 5 incorporates the development discussed in Chapters 3 and 4, toward the development of a high performance dilute nitride QW-bearing solar cells. State of the art regarding dilute nitride solar cell growth is provided, and the necessity for improving carrier extraction is indicated. The concept of *thermo-resonant tunneling* is introduced to accelerate carrier extraction in these devices. Theoretical projections of improvements in current are described, and dimensions of resonant tunneling structures are worked out. Following the work of Chapter 4, growths of some preliminary samples using the modified plasma design are described. The resulting device characteristics are highlighted showing for the first time the possibility of fabricating dilute nitride solar cells with near ideal carrier extraction and record open circuit voltage characteristics.

Chapter 6 provides a summary of their achievements, and suggestions towards implementation of these findings for the development of solar cell with efficiencies approaching or exceeding 50%. 
Chapter 2: Principles of Photovoltaic Operation

2.1 Introduction

From time immemorial, the sun has served as the sustenance of all civilization, directly through its effect on human health, and indirectly via the food and water cycles in nature. The sun’s energy supply is the main driving force behind these phenomena, which amounts to 1 kW/m^2 on the outer surface of the earth. In comparison, the utilization of the available resources for energy by mankind has remained minimal in spite of the increase over the last century (Fig. 2.1).

![Figure 2.1: The rise in energy use over the past 150 years [9].](image)

However, every hour, more energy shines onto the surface of the earth than the yearly usage of the entire planet (14 TW-yr). Thus, in comparison with the available sources of energy, both renewable and non-renewable, the sun offers a serendipitous opportunity to solve the ever-increasing energy needs of humanity.
2.1.1 Photovoltaic effect: Origins

Although the use of sunlight for as a natural heat source has had a long history, the first recorded [10] experimental observation of a direct production of electrical energy from light was the discovery by French scientist Alexandre-Edmond Becquerel in 1839, where he showed that upon shining light on it, an electric difference of potential is established between two plates of platinum immersed in an acidic electrolyte [11]. This explains the origin of the term photovoltaic combining photon (from Greek \(\text{phōs}\) meaning light) and voltaic cell of Alessandro Volta. This discovery in a liquid electrolyte was followed by the demonstration of photoconductivity by Adams and Day (1876) in solid state: selenium [12], and 8 years later, Charles Fritts [13] sandwiched selenium between a gold leaf and a metal and demonstrated the possibility of converting sunlight into electricity, creating a configuration in use to this day (Fig. 2.2).

![Figure 2.2](image1)

(a) Selenium layer attached to a metal plate, with a gold leaf placed on it, providing the first “front” and “back” contacts [13].

(b) Schematic of the first p-n junction [14].

Following a dormant period of decades, different materials like Cu/Cu\(_2\)O, CdS and Tl\(_2\)S were found to be photosensitive [15] [16]. The further crucial discovery of a junction in
high-purity silicon ingots by Russel Ohl of Bell Labs in 1941[14] showed a property of generating positive or negative photo-voltage on either side of the junction, especially when light is shone onto it. Hence the discoveries of the p-n junction diode and modern photovoltaic effect occurred simultaneously. Further improvements in Bell Labs by Pearson et al. [17], enabled a 15-fold increase in efficiency of Si-based p-n junction solar cells to obtain 6%. This led to the further development of p-n junctions, and the birth of microelectronics and modern photovoltaics. This development will now be analyzed systematically.

2.2 Photovoltaic Conversion

Photovoltaic conversion is the conversion of incoming solar radiation into usable power, or in other words, the process involves:

1. The absorption of incoming sunshine by a material
2. The generation of electrical power in the material

Step 1 involves the determination of the properties of incoming sunshine, the choice of material, as well as the strength of absorption. Step 2 involves a process called “charge-separation” where the understanding of a p-n junction as well as the electrical characteristics of the circuit is crucial. These two steps enable one to determine the overall efficiency of the conversion process, and will now be examined.

2.2.1 Sun spectrum and its properties

The sun is a star which generates radiation spanning the entire electromagnetic spectrum,
with a peak in the visible region. Comparing the spectrum with the radiation of Planck’s “black-body”, one can identify the temperature of the solar corona to be equivalent to 5800 K. The variations in solar intensity follows the time of the day, weather conditions, and the physical location of the place of interest, each one of which are accounted for in the input for solar cells.

The sun’s intensity per wavelength, or irradiance, is almost evenly split between visible (400-700 nm) and infrared (>700 nm) radiation (45% and 46% respectively). Due to the absorption by atmospheric gases and water vapor, distinct absorption bands appear in the spectrum at ground level as compared to that at the periphery of the atmosphere. To characterize this absorption, a term called air mass (AM) is used, which denotes the length of atmosphere that the light rays have to interact with on average (see Fig. 2.3). In addition, there is also a split between the direct component of solar radiation and the radiation from diffuse elements in the atmosphere such as dust and clouds. The effective spectra are shown in Fig. 2.4. The sun irradiance in the outer atmosphere is denoted as AM0. The sunlight irradiance at sea level is referred to as AM n where the number n denotes the inverse cosine of the sun zenith angle with respect to the local normal.
Figure 2.3 Schematic showing air mass (AM) as a function of angle of incidence. Typical space conditions are characterized by AM0, while AM 1.0 is used to indicate direct irradiance. AM 1.5 is most commonly used to estimate the irradiance of an average day. [courtesy LaserFocusWorld]

Figure 2.4 Comparison of extraterrestrial spectrum and AM irradiances. Global irradiance includes the average direct and diffuse components. [Data courtesy ASTM and NREL, Golden CO.]

Peak values of the sun’s intensity vary between 1353 W m\(^{-2}\) (for AM0, called the solar constant), 925 W m\(^{-2}\) (AM1) and 885 W m\(^{-2}\) (AM 1.5 G) [18].
The total photon flux impinging on a surface for a black-body radiation is given by:

\[ F(E) = \frac{2\pi \sin^2 \theta}{h^3 c^2} \frac{E^2}{e^{E/k_B T} - 1} \]

Where \( \theta \) is the half-angle subtended by the sun from the point where it is measured, \( T \) the temperature of the sun’s surface, which can range from \( 2.16 \times 10^{-5} \pi \) (at the Earth’s distance) to \( \pi/2 \), depending on what is called “solar concentration” (1 sun-46200 suns). \( E \) is the energy of the photon, \( h \) is Planck’s constant, \( c \) is the speed of light, and \( k_B \) the Boltzmann constant.

### 2.2.2 Semiconductor band-gap

Once the properties of solar radiation are determined, choice of a suitable material capable of absorbing it is necessary. Ever since their discovery in 1833 by Faraday, one property of semiconductors has been their defining feature – an increase in conductivity upon heating by several orders of magnitude. Since it is a short step from excitation via heat to excitation via light, the mechanism and magnitude of energy absorption of a semiconductor must be described.

Semiconductors are materials that have properties intermediate between metals, which are excellent electrical conductors, and insulators. Study of electrons and holes [19] in metals using Fermi-Dirac statistics showed that the energy levels of electrons can be represented as bands [20][21], and the energy of free-electrons are given by:
\[ E = \frac{\hbar^2 k^2}{2m_e} \]

Where \( \hbar \) is the Planck’s constant divided by \( 2\pi \), \( k \) is the wave-vector and \( m_e \) is the effective mass of the electron. Utilizing the work of band theory [22] in both metals, semiconductors and insulators, it was proposed [23] that the magnitude of separation of the bands (Fig. 2.5) determined the property of semiconductors.

![E-k band diagram](image)

Figure 2.5 Schematic of E-k band diagram indicating the gap (\( \Delta E \)) in a typical semiconductor between the occupied (bold) and empty electronic levels, called valence band (VB) and conduction band (CB) respectively. For metals, VB and CB overlap, while for insulators, \( \Delta E >> 5 \text{eV} \).

The conduction of electrons can be described empirically by:

\[ \sigma = \sigma_0 e^{-\Delta E/\kappa_B T} \]

Here \( \sigma \) is the conductivity, and \( \sigma_0 \) is a constant for a specific material. The exponential factor explains the origin of the anomalous decrease of resistance with change in
temperature, and introduces the quantity called *band-gap* ($\Delta E$), relative to the thermal energy $k_B T$.

A different, and more direct, approach to understanding the band gap is a study of optical absorption of different materials. When the energy of the incoming photon $h\nu < \Delta E$, the material is transparent to it, while when $h\nu \geq \Delta E$, it is absorbed. This process causes an *internal photoelectric effect*, where the electrons excited by light do not leave the bulk of the material, but continue their motion inside. The transitions have the possibilities shown in Fig. 2.6.

![Figure 2.6: Schematic of absorption of incoming photon when (a) $h\nu_1 < \Delta E_g$ where the material is transparent to the photon, (b) $h\nu_2 = \Delta E_g$ which transfers an electron from the filled valence band to conduction band, leaving a hole, and (c) $h\nu_3 > \Delta E_g$ where the electron relaxes from an excited state by transfer of momentum via phonons in the crystal lattice ($\hbar k$) and energy $\Delta E_{th}$ called *thermalization*.](image)

The explanation for the presence of phonons in the transition to the band edge has to do
with the shape of the energy band in k-space, which further helps define two types of band-transitions: direct and indirect. More details are provided on pg 52, ref [24].

The value of the band-gap, typically measured in electron-volts (eV) is crucial in determining the choice of material for solar absorption (0-5 eV). However, in addition to the value of energy at which absorption occurs, the strength of the absorption requires knowledge of the number of electronic transitions that occur at that energy, which in turn depends on the density of states.

2.2.3 Density of States and Quantum Confinement

The de-Broglie wavelength of an electron λ is inversely proportional to its momentum
given by $\lambda = \frac{h}{p}$. In bulk, or three-dimensional (3D) materials the motion of electrons is not restricted as the de-Broglie wavelength of the lattice is much smaller than that of the electron, but as the size of the materials becomes small enough in at least one dimension to be compared with the wavelength of the electron then the electron motion becomes restricted. These structures of small size are called low-dimensional structures, and the process is called quantum confinement.

![Figure 2.8 Schematic [25] of semiconductors in decreasing order of dimensionality: (a) bulk 3D (b) quantum well (2D) (c) quantum wire (1D) and quantum dot (0D). Quantum confinement is achieved in 0, 1, 2, and 3 dimensions respectively.](image)

It is possible to calculate the conductivity of each of these structures by analyzing the occupancy of their bands. A fully filled valence band and a fully empty conduction band imply insulating behavior. Hence, if “$n$” is the number of electrons (or any charge carrier) that can occupy the conduction band:

$$n = \int_{E_{CB}}^{E_{max}} \rho(E)f(E)dE \quad 2.4$$

Where $\rho(E)$, or the density of states (DOS) are calculated by counting the number of states per energy $N(E)$ per unit volume of real space and is given by $\rho(E) = \frac{dN(E)}{dE}$.
while $f(E)$ indicates the probability of occupation or electronic distribution function, which is also called the Fermi-Dirac distribution [26]:

$$f(E) = \frac{1}{1 + e^{E-E_F/k_B T}}$$

Here $E_F$ is the highest occupied energy level in a fermionic system. $N(E)$ is calculated by obtaining the number of unit volume elements within a dimension dependent range $E_F$ in reciprocal $k$-space, given by:

$$N(E) = \frac{4k^3}{3\pi} \quad (3D)$$

$$N(E) = \frac{k^2}{2\pi} \quad (2D)$$

$$N(E) = \frac{k}{\pi} \quad (1D)$$

$$N(E) = \begin{cases} 2, & k < k_F \\ 0, & k \geq k_F \end{cases} \quad (0D)$$

Where $k_F = \sqrt{2mE_F/\hbar^2}$ and $= \sqrt{2mE/\hbar^2}$. Hence, the number of states obtained for bulk (3D) materials is proportional to $k^3$, for 2D materials like quantum wells proportional to $k^2$, and so on. These numbers give the strength of the absorption for a transition for each configuration, which will be utilized in Chapter 3. The density, obtained by differentiating $N$ w.r.t $E$, is given by:
\[
\rho_{3D}(E) = \frac{1}{2\pi^2} \left(\frac{2m_{\text{eff}}}{\hbar^2}\right)^{3/2} \sqrt{E - E_C} \ast \Theta(E - E_C)
\]
\[
\rho_{2D}(E) = \frac{m_{\text{eff}}}{\pi\hbar^2} \ast \Theta(E - E_C)
\]
\[
\rho_{1D}(E) = \left(\frac{2m_{\text{eff}}}{\hbar^2}\right)^{1/2} \frac{1}{\pi(E - E_C)^{1/2}} \Theta(E - E_C)
\]
\[
\rho_{2D}(E) = 2\delta(E - E_C)
\]

Where \(\Theta(E - E_C)\) denotes the step function as in the last equation of Eq. 2.5.

Energy level solutions of electrons in a quantum confined system have the form of “particle in a box” i.e., if \(L_x\) is the ‘x’ dimension of confinement, we have:

\[
E_{(k_x,k_y,n_z)} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 k_y^2}{2m} + \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \quad (2D)
\]

\[
E_{(k_x,n_y,n_z)} = \frac{\hbar^2 k_x^2}{2m} + \frac{\hbar^2 \pi^2}{2m} \left(\frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \quad (1D)
\]

\[
E_{(n_x,n_y,n_z)} = \frac{\hbar^2 \pi^2}{2m_{\text{eff}}} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \quad (0D)
\]

Thus, the density of states for the various energy levels reduces significantly with the reduction of each dimension (Fig 2.9).
Figure 2.9: Density of states for (a) 3D bulk material (b) 2D “quantum well” structure (c) 1d “quantum wire” or nano-wire structure, and (d) delta function for 0D or “quantum dots”

From Eq. 2.3, 2.4 and 2.6 the carrier concentration of electrons can now be determined:

\[ n_e = N_c \exp \left( \frac{E_F - E_C}{k_B T} \right) = 2 \left( \frac{2\pi m_e k_B T}{\hbar^2} \right)^{3/2} \exp \left( \frac{E_F - E_C}{k_B T} \right) \]  

2.9

Similarly the expression for holes can be obtained as well, using \( E_V \) for valence band energy:

\[ p_h = N_V \exp \left( \frac{E_V - E_F}{k_B T} \right) = 2 \left( \frac{2\pi m_h k_B T}{\hbar^2} \right)^{3/2} \exp \left( \frac{E_V - E_F}{k_B T} \right) \]  

2.10

In a semiconductor without impurities, \( n_e = p_h = n_i \), also called the “intrinsic” carrier concentration. The Fermi level energy can easily be determined for equilibrium conditions as:

\[ E_F = \frac{E_C + E_V}{2} + \frac{k_B T}{2} \ln \left( \frac{N_V}{N_C} \right) \]  

2.11

Where \( m_e \) and \( m_h \) are given by the curvature of E-k diagram [19] at \( k = 0 \), also called effective mass, and \( N_V \) and \( N_C \) are the occupancy of valence (hole) and conduction (electron) bands respectively. Thus, the Fermi level for an intrinsic semiconductor lies in the middle of \( E_V \) and \( E_C \).
When light is incident on an electronic semiconductor, as the electrons get excited from the valence to the conduction band leaving a positively charged hole in the valence band, it is important to separate the electrons and holes before they lapse back to their equilibrium positions. Hence, an asymmetry in potentials has to be created between the holes and the electrons. There are various ways to achieve this, including metal-semiconductor contact, differences of temperature, and semiconductor-semiconductor contact. The last option will be examined here, i.e. via the formation of a p-n junction.

2.2.4 The p-n junction

Intrinsic semiconductors can be doped with small amounts of impurities, which vastly change their electrical characteristics. This is done by introducing elements whose valence lies either +1 or -1 from the valence of the intrinsic element, called donors or acceptors respectively. For example, GaAs which is a III-V semiconductor, when doped with Si (group IV) or Be (group II) generates donors (electrons) or acceptors (holes) respectively, as the dopants replace the valency III of Ga.

Figure 2.10: Position of Fermi level in intrinsic semiconductor lies midway within the band-gap.
Figure 2.11: Generation of donor and acceptor levels by the addition of dopants to a material of band-gap $\Delta E_g$, moving the Fermi level $E_F$ towards (n-type) and away (p-type) from the conduction band.

This generates either an \textit{n-type} GaAs or a \textit{p-type} GaAs. Increasing the population of electrons raises the position of the Fermi level energy (also called chemical potential due to its dependence on carrier population) due to the presence of the \textit{donor levels} ($E_D$) while the opposite is the case with respect to the \textit{acceptor levels} of holes ($E_A$). When a p-type and n-type material are put in contact with one another, the Fermi levels of the two sides equalize, generating a potential difference between the band gap on either side of the junction. This asymmetry of potential, and the corresponding built-in electric field, sweep the electrons and holes generated by incoming light in opposite directions (electron and hole currents), creating the p-n junction photovoltaic effect.
Figure 2.12 The p-n junction configuration of GaAs showing built in electric field, and opposite motion of the electrons and holes.

The action of a p-n junction hence creates a potential difference, which can be approximated by the difference in the non-equilibrium Fermi-levels of p- and n-sides of the junction as shown in Fig. 2.12. For convenience, these non-equilibrium Fermi-levels are referred to as “quasi-Fermi levels” and the potential difference is given by:

\[ \Delta \mu = k_B T \ln \left( \frac{N_C}{N_V} \right) \]  

2.2.5 Carrier Generation and Recombination

Generation of carriers takes place as a result of incoming photon flux of photons with energy exceeding the band-gap and available electron energy states in the semiconductor. For a transition from electron energy 1 to a level 2 with density of states \( \rho_2 \), the
probability of transition is given by the Fermi Golden Rule [27]:

$$T_{12} = \frac{2\pi}{\hbar} |M_{12}|^2 \rho_2$$

2.13

Where $M_{12}$ is the matrix element between quantum mechanical states $|1\rangle$ and $|2\rangle$ of the perturbation due to the incoming photon. As already indicated, the transition of the electron can occur at $k=0$ (direct) or at $k\neq 0$ (indirect transition). Combining this with the calculation of density of states derived for bulk material, the carrier generation for direct transitions can hence be represented by the absorption as [24]:

$$\alpha(E) \propto |M_{12}|^2 (E - E_g)^{1/2}$$

2.14

Where $E_g$ is the band-gap. For indirect transitions, the absorption is a function both of the incoming photon energy $E$ as well as the phonon energy change $E_p$. This gives a dependence [28][29]:

$$\alpha(E) \propto |M_{12}|^2 (E + E_p - E_g)^2$$

2.15

Thus far, the generation of carriers via dependence on doping and band-gap has been considered. Under illumination of a p-n junction, there is motion not only of majority carriers, i.e., electrons in n-type region and holes in p-type, but also the motion of minority carriers, i.e., holes in n-type region or electrons in p-type [30]. Hence, there is a finite probability of recombination of the separated carriers, releasing the energy back into the material. Recombination has been discussed extensively in literature [31][32][33], so here we only briefly discuss the various possible recombination mechanisms.
There are two main types of recombination: radiative and non-radiative. Radiative recombination occurs as the exact reverse of direct band-gap energy transition, i.e., the energy absorbed is released as radiation due to the decay of the electron from the conduction band to the valence band. Hence this phenomenon is more important in direct band-gap semiconductors such as most III-V’s. Non-radiative recombinations occur in mainly two ways: Auger recombinations and Shockley-Read-Hall recombinations [34], which are more common in indirect band-gap semiconductors such as Si and Ge. These bulk processes are schematically represented in Fig. 2.13. In addition, recombination also occurs at the surface of the semiconductors due to the inevitable crystal state discontinuities, which is characterized by the *surface recombination velocity*.

![Figure 2.13: Recombination processes in semiconductors – Radiative (via emission), Shockley-Read-Hall (SRH, via a defect or trap level) and Auger recombination (via thermalization of excited carrier).](image)

The effective recombination lifetime in a junction, called *minority carrier lifetime*, is
given by [35]:

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{SRH}}} + \frac{1}{\tau_{\text{Auger}}} + \frac{1}{\tau_{\text{surf}}} \tag{2.16}
\]

With these basics in place, the choice of a material can be made and a description of actual solar cell performance can be given. The characteristic distance a minority carrier is likely to travel in a semiconductor without recombining is called its diffusion length, given by:

\[
L = \sqrt{D\tau_{\text{eff}}} \tag{2.17}
\]

Where D is the diffusivity or diffusion coefficient of the material.

### 2.3 Solar Cell Device Design

#### 2.3.1 Ideal p-n junction device

As described, a p-n junction forms the core of a solar cell. In terms of circuit elements, an ideal junction can be represented as a combination of a current generating element \( (I_p) \) with a diode in parallel \( (I_D) \), supported by an external load \( (R) \) (See Fig. 2.14). A potential difference \( V \) develops between the ends of the cell, and under open circuit conditions, this value is called *open circuit voltage* \( (V_{OC}) \) while the current at \( R=0 \) is called *short circuit current* \( (J_{SC}) \). These two parameters provide the maximum possible voltage and current for the device respectively. All stray resistances are assumed to be zero, the contact between the metal and semiconductor on either side of the junction are assumed to be loss-less.
Figure 2.14: Schematic of Solar Cell as current source+diode, indicating the directions of photon current \( I_p \) and diode (dark) current \( I_D \), under load \( R_1 \).

The current of this ideal solar cell is \([36]\):

\[
I(V) = I_p - I_D = I_p - I_0(e^{\frac{qV}{k_BT}} - 1)
\]  

2.18

Where \( I_D \) is the dark current of the ideal diode, \( I_0 \) the saturation current and \( I_p \) the illumination current. The maximum current is referred to as short circuit current (\( I_{sc} \)) while the maximum voltage generated between the ends is referred to as the open circuit voltage (\( V_{oc} \)). They are given by:

\[
I_{sc} = I_p
\]  

2.19

\[
V_{oc} = \frac{k_BT}{q} \ln\left(\frac{I_{sc}}{I_0} + 1\right)
\]

The photon current \( I_p \) induced upon illumination is given by:

\[
I_p = qA \int_0^\infty F(E)Q(E)dE
\]  

2.20

Where \( F(E) \) is given the incoming photon flux given by either by equation 2.1 (or by data tables for AM1, AM1.5 etc) and \( Q(E) \) is the quantum efficiency of the cell defined as...
the probability that an incident photon of energy $E$ will deliver one electron to the circuit.

The saturation current $I_0$ for a p-n diode is given by [37]:

$$I_0 = qN_C N_V A \left( \frac{1}{N_A} \sqrt{\frac{D_n}{\tau_n}} + \frac{1}{N_D} \sqrt{\frac{D_p}{\tau_p}} \right) \exp \left( \frac{E_g}{k_B T} \right)$$  \hspace{1cm} 2.21

Here $N_C$ and $N_V$ are conduction and valence band density of states as obtained by equations 2.8 and 2.9, $N_A$ and $N_D$ are acceptor and donor level density of states, $A$ is the area of the cell, $D_p$ and $D_n$ are the diffusion coefficients, $\tau_p$ and $\tau_n$ are the minority carrier lifetimes in the semiconductor with band-gap $E_g$. The current voltage characteristics under illumination and in the dark are given in Fig. 2.15, showing the curve displaced due to current generation by the solar cell.

![Figure 2.15: I-V characteristics of a solar cell in dark and illuminated conditions. $(V_m, I_m)$ corresponds to the maximum power point, and the shaded region is used to calculated the fill](image-url)
The maximum power point of a solar cell is obtained by evaluating the solution of \( d(IV)/dV = 0 \), and the fill factor (a measure of the ideality of the diode) is given by:

\[
FF = \frac{I_{m}V_{m}}{I_{sc}V_{oc}}
\]

2.22

Hence, the overall efficiency of a solar cell is given by the ratio of output power at the maximum power point and the incident power of the incoming light:

\[
\eta = \frac{I_{sc}V_{oc} \times FF}{P_{s}}
\]

2.23

Where \( P_{s} \) is the total incoming photon power.

2.3.2 Single Junction Solar Cells

The simplest device that can be considered for a photovoltaic cell is a single junction, p-n diode made of a semiconductor whose bandgap matches the sun’s spectral range (see Fig.2.16). Decreasing the band-gap increases the amount of energy lost by thermalization, while increasing the band-gap increases transparency photon losses. Hence, it is important to choose a material where efficiency losses due to these two competing phenomena are minimized. Additionally, a direct-band-gap semiconductor has a shorter diffusion length, higher electron mobility and greater absorption coefficient, while an indirect-band-gap material has a longer diffusion length. Traditionally, silicon has been a good choice due to its band-gap being 1.1 eV, yet its poor absorption properties require a much thicker cell (200 \( \mu \)m) to absorb all the light as compared to a direct band-gap semiconductor like GaAs (3 \( \mu \)m).
A typical GaAs (band-gap at 300 K: 1.42 eV) solar cell has the structure shown in Fig. 2.17. An anti-reflecting coating (ARC) at the prevents reflection losses from the front surface of the device. A metallic grid, generally made of gold or silver, serves as the top contact, and also introduces losses due to grid-shadowing. Back contact is also metallic, created by thermal evaporation. The emitter and base of the device are the p- and n-junctions respectively, generally doped with Be (p) and Si (n). The Al_{0.8}Ga_{0.2}As layer at the top is a wide-band gap material serving to restrict surface recombination of carriers, called the *window layer*. An Al_{0.2}Ga_{0.8}As layer at the back creates an electric field, called a *back surface field* (BSF) that repels the minority carriers towards the junction. The highly doped p-GaAs on top forms an ohmic contact with the front contact.
Figure 2.17: Typical single-junction GaAs solar cell, with anti-reflective coating (ARC) and front contact on the top, and a metallic back contact. AlGaAs layer serves as the Back Surface Field (BSF) to repel minority carriers towards the p-n interface. [39]

An estimate for the efficiency of single junction solar cell is obtained by the Shockley Queisser model [40], also called the *detailed balance* model. Detailed balance model is an ideal model that does not take into account the physical properties of a semiconductor, and assumes that every electron-hole pair generated is extracted from the cell. The only loss mechanism in this case is the black-body emission of the cell.

Absorbed and incident flux for a solar cell, with sun temperature $T_s$ and band-gap $E_g = h\nu_g$ are given by:

$$Q_s = Q(v_g, T_s) = \frac{2\pi}{c^2} \int_{v_g}^{\infty} \frac{v^2 dv}{\exp\left(\frac{hv}{kT_s}\right) - 1} = \frac{2\pi(kT_s)^3}{h^3 c^2} \int_{x_g}^{\infty} \frac{x^2 dx}{\exp(x) - 1}$$

2.24
The ratio \( Q_s/P_s \) would give the maximum possible efficiency of such a system. However, due to the principle of detailed balance, radiative recombination can never be reduced to zero, and is the energy emitted at a temperature \( T_c \) of the solar cell:

\[
Q_c = Q(v_g, T_c) = \frac{2\pi(kT_c)}{h^3c^2} \int_{x_g/x_c}^{\infty} \frac{x^2}{\exp(x) - 1} dx
\]

This gives the I-V characteristics of this ideal cell and thereby the open circuit voltage:

\[
V_{OC} = \frac{k_B T_c}{q} \ln \left( \frac{I_{SC}}{I_0} + 1 \right) \approx \frac{k_B T_c}{q} \ln \left( \frac{f Q_s}{Q_c} \right)
\]

Where \( f \) is factor including the effect of concentration and the ideality of the cell. The maximum experimental efficiency of a single junction solar cell, both for ideal absorber and for different materials is given in Fig. 2.18, as calculated with the Shockley-Queisser model.
Figure 2.18: (a) Efficiency of a single junction showing loss mechanisms of an ideal cell and (b) efficiency of different single junction solar cells under AM1.5 G spectrum using Detailed Balance model as compared with experimental values [41]. Note the large difference especially for a-Si:H, CdTe and CIGS materials whose crystalline quality is lower than IV or III-V solar cells.

The highest value reported for III-V single junction solar cells is for GaAs under standard
conditions (28.8%, AM1.5) as well as under concentration (29.1%)[42].

### 2.3.3 Multi-Junction Solar Cells

One way to go beyond the Shockley-Queisser limit is to reduce transparency losses in the solar cell, by stacking multiple junctions on top of each other such that the second junction lies in the transparency region of the first, and the third lies in the transparency region of the second, and so on. The individual sub-cells can be connected via transparent conductors (i.e. tunnel junctions). Constraints in the design of multi-junction solar cells involve lattice-matching, and current matching. Since each sub-cell is grown epitaxially on the previous one, a large lattice mismatch between the cells introduces defects which act as recombination centers and hence sap the efficiency of the cell. The relationship between band-gap and lattice-constant (Fig. 2.19) is used to select suitable species.

![Band-gap vs lattice constant](image)

**Figure 2.19** Band-gap vs lattice constant for various semiconductors, where the bold and dashed lines indicate the properties of alloys with direct and indirect transitions respectively. The system for multi-junction is highlighted, where each material has an almost identical bandgap.

An example of such a system, utilizing InGaP/Ga(In)As/Ge system is shown in Fig. 2.20.
Figure 2.20: Schematic of a 3-junction solar cell, showing the corresponding spectral absorption. Light shines in from the top, and the lower Sub-cell lies in the transparency region of the upper Sub-cell.

The voltage and current of a multi-junction cell is the same as a set of resistors in series:

\[ V = \sum_i V_i \quad 2.28 \]

\[ I_{MJ} = \min (I_i) \quad 2.29 \]

Recent experimental results of high efficiency cells in literature are given in Table 1 [42]. Due to the significant improvement over single-junction, recent efforts to obtain high efficiency solar cells have focused on multi-junction configuration, in particular to increase the number of sub-cells without increasing the material growth issues (such as defects, costly growth, contact issues) that come with growing multiple junctions.
Table 1

<table>
<thead>
<tr>
<th>Type</th>
<th>Efficiency (1 sun)</th>
<th>Efficiency (300-500 sun)</th>
<th>Ideal Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>2J (InGaP/GaAs)</td>
<td>31.4%</td>
<td>34.6%</td>
<td>42%</td>
</tr>
<tr>
<td>3J (InGaP/GaAs/InGaAs)</td>
<td>35.8%</td>
<td>44.3%</td>
<td>51%</td>
</tr>
<tr>
<td>4J (InGap/GaAs/InGaAs/Ge)</td>
<td>33.6%</td>
<td>NA</td>
<td>56.8%</td>
</tr>
</tbody>
</table>

As an example, under conditions of full extraction, the efficiency of 4 Junction cell as a function of band-gap optimization of 1\textsuperscript{st} and 3\textsuperscript{rd} subcell is shown in Fig. 2.21. As can be seen, there is a requirement for a sub-cell close to 1eV in order to achieve high efficiencies.

![Diagram of 4 Junction Solar Cell Efficiency](image)

Figure 2.21: Efficiency optimization by varying band-gap of 1\textsuperscript{st} and 3\textsuperscript{rd} cell in a 4-junction setup. The ideal combination was found to be (2.14 eV, 1.02 eV).

2.3.4 Multi-Quantum Well (MQW) Solar Cells

The depletion region of the solar cell is where, driven by the drift field, maximum charge
separation occurs, and hence p-i-n solar cells can be fabricated, where an intrinsic (undoped) semiconductor is inserted into the p-n junction to improve carrier collection. There is however a constraint on the size of this intrinsic region, as the electric field strength reduces with increased thickness.

Hence, an alternative to increase the efficiency beyond the Shockley Queisser limit is to enhance the absorption in the transparency layer of a single-junction solar cell, i.e. by introducing quantum nanostructures within this intrinsic region (called i-region). As described in Section 2.2.3, density of states of quantum wells (2D) is the highest among different nanostructures, hence a good candidate from optical absorption standpoint. A schematic of the structure and carrier motion in quantum well solar cells is given in Fig. 2.22.

Figure 2.22 (a) Schematic of carrier transition in a p-i-n MQW solar cell. $E_a$ is absorption, $E_{ph}$ the incoming photon energy, $E_b$ is the band-gap and $V$ is quasi-fermi level separation. Electrons and holes are transported due to thermal excitation from the QW.[43] (b) Schematic of a p-i-n MQW structure, from patent [2].

Absorption of MQW solar cells have showed significant below band-gap quantum
efficiency and \( I_{sc} \) improvement over standard p-i-n solar cells \[44][45].

Voltage enhancement was observed in QW solar cells \[46], and it was attributed to a drop in dark current of the diode structure. This is possibly because our assumptions about the positions of quasi-fermi level are not completely valid in the quantum well region.

In order to obtain 1eV lattice matches solar cells, dilute nitride MQW solar cells have been proposed \[2]. Any further discussion this design requires better understanding of absorption properties of dilute nitrides quantum nanostructures, which would be described in Chapter 3.
2.4 Summary

Following a short historical discussion, in this chapter a brief overview basic solar cell operation has been given, beginning with the physics of a p-n junction. Photon absorption, carrier generation and recombination mechanisms have been outlined, and the resulting device behavior has been described, using examples of single-junction, multi-junction, and quantum nano-structured devices.
Chapter 3: Simulation of Dilute Nitride MQW Multi Junction Solar Cell

3.1 Dilute Nitride alloys of III-V semiconductors - An overview of their properties

The material alloy obtained by the addition of a small percentage of nitrogen (typically <5%) to a conventional III-V semiconductor is called a “dilute nitride”. The introduction of N in the alloys is accompanied by a large reduction in the bandgap [47] which has enabled a tailoring of the band structure of III-V semiconductors, leading to the development of new types of light emitting diodes, edge emitting lasers, semiconductor optical amplifiers etc. [48]–[50] In addition to the band gap, various physical properties of dilute nitride semiconductors undergo drastic changes with the introduction of nitrogen. Understanding this would require an overview of the material behavior, particularly with respect to those parameters that are vital to the structure of a solar cell. Of particular interest to us is the use of the anomalous band contraction to obtain 1eV bandgap structures from GaAs solar cells (1.42 eV) [7]. In this section a description of the anomalous bandgap behavior would be given, followed up by the other variations seen in carrier properties, such as mobility and effective mass of electrons, both of which are vital for solar cells. These experimentally observed variations will be described in the next section along with a phenomenological model to describe their evolution as a function of the N-content of the alloy, called the band anti-crossing (BAC) model.
3.1.1 Anomalous Band Contraction of Dilute Nitrides: experimental and phenomenological observation

The anomalous band contraction of dilute nitrides was first investigated in GaP [51] where the effect of the incorporation of N showed a redshift as opposed to the expected blueshift in the bandgap. This was further reinforced by the pioneering work of Weyers and Sato [3], and Kondow [52] who confirmed a significant redshift of photoluminescence with introduction of nitrogen in GaAs. The redshift was contrary to expectations from the prevailing Vegard’s law. According to this law, the expected bandgap of GaAsN had to be within that of GaAs (1.42 eV) to GaN (3.2 eV). A large bowing coefficient was observed even when the parabolic extrapolation was used, and Vegard’s law was seen to be insufficient even to obtain the lattice constant of dilute nitrides accurately [53]. A strong redshift of up to 100meV per percent of N called for a different explanation for the redshifts.

Figure 3.1. Expected bandgap variation [54] of III-V-N materials from Vegard’s law
Figure 3.2 Unexpected shrinkage of III-V-N bandgap with the addition of nitrogen [55].

This bandgap tuning property of dilute nitrides made them a very attractive topic for novel applications in semiconductor technologies and most relevantly, in solar cells. It was hence of utmost importance to understand the precise nature of the transition, and various attempts have been made in the literature. The transition from N-doping to alloy formation was hence investigated [56] and the cause for the bandgap shift has been tentatively identified as the movement of a “resonant N-level”, i.e., an energy state of nitrogen-complex lying within the conduction band, from the conduction band into the bandgap [57][58]. Among other explanations, the formation of N-related impurity levels below the band gap has also been suggested as the reason for bandgap reduction [59]. The anomalous nature of this contraction was also reinforced by its reduced sensitivity
(as compared to GaAs) under hydrostatic pressure [60] and temperature [61].

3.1.2 Minority Carrier Properties in Dilute Nitrides

Minority carrier diffusion length is a key parameter for solar cell performance, as it determines how far the carrier moves in the lattice, on average, before recombining and emitting the absorbed energy. Due to the strong variation induced in the crystal by N-incorporation, a drastic variation in minority carrier properties was observed in dilute nitrides [6], [7]. For instance, electron diffusion length for GaAs can be 10 µm or more, whereas for Ga(In)AsN, it is restricted to 0.1-1 µm range. There are primarily two ways in which the diffusion length is determined.

One way is to obtain the internal quantum efficiency (IQE) and the absorption coefficient ($\alpha$) of a p-n junction, and fit it with the appropriate model for extracting the diffusion length $L$. The IQE for a p-n junction with a depletion width $W$ is given by [37]:

$$QE(\lambda) = \frac{\alpha L \exp(-\alpha W)}{1 + \alpha L} + [1 - \exp(-\alpha W)]$$

$W$ is determined from an alternative method such as capacitance-voltage profiling, and this allows us to extract $L$. Further studies of hole and electron diffusion lengths by this method for MBE-grown samples have provided values of 0.03 µm ($L_h$) and 0.25 µm ($L_e$). [62]

A second method is to utilize the mobility and carrier lifetime measurements to obtain the diffusion length. The relevant equation is [31]:

$$\ldots$$
Here, $\mu$ is the carrier mobility, $\tau$ the carrier lifetime, and $T$ the ambient temperature of the crystal. Independent determination of the carrier lifetime, done by time-resolved photoluminescence studies (TRPL) has given values of 0.2-1 ns for dilute nitrides with $1.5% < [N] < 2.6%$ [63], which is nearly two orders of magnitude lower than that of GaAs. Meanwhile, the carrier mobility is determined by Hall effect, where it has been observed that both $p$ and $n$ type mobilities in dilute nitrides drop significantly upon introduction of nitrogen [5], [64]. In contrast to values of highest mobility in GaAs (8500 cm$^2$ V$^{-1}$s$^{-1}$), the range of reported values for Ga(In)AsN is 100-300 cm$^2$ V$^{-1}$s$^{-1}$ for $[N]=2\%$, and remain very low. Hence the diffusion lengths obtained in this method are consistent (100-fold reduction) with the previous method, and we can say that carrier diffusion length drops sharply (20 nm) with the introduction of nitrogen.

3.1.3 Effective Mass

In contrast to the absolute mass of the charge carriers generally used in atomic physics, in semiconductors the “effective mass approximation” is generally used, where the variations in the crystal potentials are incorporated into the mass of the charge carriers. Effective mass plays a vital role in determining semiconductor properties, influencing the quantum confinement energies, optical dipole matrix elements, band filling, carrier mobility, absorption coefficients etc. In addition, it serves as a sensitive way of determining the band structure of the material, as it is determined by the dispersion of the
bands. Unlike the predictable reproducibility of the giant band-gap bowing, possibly no other parameter of dilute nitrides has had the wide range of variability as the effective masses of both electrons and holes. Upon introduction of nitrogen, a sudden increase in electronic effective mass is seen, from its value in GaAs (0.067 m\textsubscript{e}) to anywhere between 0.08 m\textsubscript{e} to 0.4 m\textsubscript{e} within the addition of 4\% of N (See Fig. 3.3) However, most techniques converge upon m\textsuperscript{*}\textsubscript{e} = 0.1 m\textsubscript{e} for Ga(In)AsN, which is at least 30-40\% larger than that of GaAs [65].

![Figure 3.3 Scatter of values for the Effective Mass [65]](image)

3.1.4 Attractiveness of dilute nitrides for PV absorbers

Using dilute nitrides in solar cells is difficult as their high effective masses and short
carrier lifetimes are the opposite of what is required for efficient photo-conversion. In fact, other than the band-gap and possible lattice-matching, all semiconductor parameters appear disadvantageous. The reason for using them lies in the fact that high effective mass of dilute nitrides makes them ideal absorber materials, provided the carriers are extracted as quickly as possible without further use of bulk dilute nitride material. This is the motivation for using dilute nitride quantum wells within intrinsic GaAs, since the typical confinement lengths of quantum wells are < 10 nm, enabling carrier escape away from GaAs p-n junction, which generally occurs by thermionic means and hence is insensitive to the diffusion length in the well material. Additionally, doping issues [5] which had been encountered with dilute nitrides, such as amphoteric doping of silicon in GaAsN, are bypassed entirely by restricting the quantum wells to the intrinsic region. Hence it is necessary to design a quantum well system for optimum absorption and optimum carrier escape, the first of which will be described in this chapter while the latter would be described in Chapter 5.

3.2 Predicting Dilute Nitride Properties: Band Anti Crossing Model

In addition to the increase in effective mass already discussed, the presence of a highly localized acceptor-like level $N_x$ in the vicinity of the conduction band [58], [66] as well as a second energy state $E+$ that increased with the incorporation of nitrogen [58] were observed. Based on these observations, in 1999 Shan, et al. [67] proposed a model called “band anti-crossing (BAC) model” to explain the general reason for band-gap reduction in dilute nitrides.
According to this model, incorporation of nitrogen immediately creates highly localized energy states within the semiconductor matrix due to the distortion of the lattice by nitrogen, and this creates a resonant level $N_x$ that lies above the conduction band minimum of the host crystal. The interaction between this level and the conduction band minimum generates two split levels, $E_-$ and $E_+$, which move downward and upward respectively with increased concentration of nitrogen. The movement of $E_-$ causes the large shrinkage of the band gap. The valence band is taken to be relatively unperturbed. The matrix representing the interaction of $N_x$ with energy $E_N$ and the conduction band with energy $E_{CB}$ is given by:

$$
\begin{bmatrix}
E(k) - E_{CB}(k) & V_{nm}
\end{bmatrix}
\begin{bmatrix}
V_{nm}
\end{bmatrix}
E(k) - E_N(k) = 0
$$

3.3

Here $V_{nm} = C_{NM} \sqrt{x}$, is the interaction between the two states with a coupling constant $C_{NM}$ and for a nitrogen concentration $x$. The solution to this equation can be written as:

$$
E(k)_{\pm} = \frac{1}{2} \left( E_N(k) + E_{CB}(k) \pm \sqrt{[E_{CB}(k) - E_N(k)]^2 + 4V_{nm}^2} \right)
$$

3.4

Schematically the interaction can be represented as shown in Fig. 3.4.
Figure 3.4 Solid lines show conduction band dispersion calculated using the two-level band-anticrossing model. Dashed line: host matrix conduction band dispersion; dotted line: N resonant defect energy level, (from [68])

When the band gap is fit with previous experimental results [3], [52] using the BAC model, we obtain, as shown in Fig. 3.5, the parameters $E_N=1.65$ eV and $C_{NM}=2.7$ eV.

Figure 3.5 Comparison between the experimentally observed (from [3], [52]) data and calculated bandgap reduction of GaAsN as a function of nitrogen concentration.

The effective mass of the electron at $k=0$, in the parabolic approximation is given by:
Where $m_0$ is the effective mass of electron in GaAs = 0.067 $m_e$. It can be seen clearly from Fig. 3.4 that there is a flattening of the band at $k=0$, from which one would expect, using Eq.3.5, an increase in the effective mass, of up to $0.1m_e$ for 1% N [69]. This feature is hence in line with the experimentally observed increase.

Mobility is also expected to decrease according to the BAC model for high concentrations [70]. The consistency between experimental facts and the BAC model, combined with its simplicity, hence makes it an attractive candidate for use in modeling dilute nitride absorption for solar cells. This would be described in the following section.

### 3.3 Quantum Confinement and Absorption Coefficient

As discussed in earlier, the design of interest to us is the dilute nitride multi quantum well structure, inserted into the i-region of a p-i-n GaAs solar cell (see schematic in Fig 3.6). Quantum wells create confinement and provide a finite density of states below the bandgap, facilitating creation of electron-hole pairs.
Figure 3.6 Schematic of band diagram of GaAs(p)/GaAsN/GaAs(i)(MQW)/GaAs(n) photovoltaic structure. The effective bias is due to the band offset due to p and n doping.

Calculation of the absorption coefficient of this structure involves (a) the determination of the band structure of the system, (b) the determination of the confined energy levels of the system and (c) determination of the optical absorption of the entire p-i-n system, followed by a study of further modifications to the QW system.

3.3.1 Band Structure Calculation

The value of the conduction band energy has already described with respect to the band anti-crossing (BAC) model. Since both GaAs and GaAsN are direct band gap materials, our interest in the band structure is primarily in the vicinity where wave-vector $k=0$. Hence among the different possible methods for the calculation of the band structure, such as empirical pseudo-potential method, tight binding method, Green’s function method, etc. [28] the focus here would be on the $k\cdot p$ method [71], in conjunction with the
Luttinger-Kohn model [72]. This method is briefly described here.

The origin of the term “$k \cdot p$” is the expansion of the momentum expression in the following Hamiltonian:

$$\left( \frac{p^2}{2m} + \frac{\hbar k \cdot p}{m} + \frac{\hbar^2 k^2}{2m} + V \right) \phi_{nk} = E_{nk} \phi_{nk}$$

The steps of developing $k \cdot p$ method are:

1. Substitute the Bloch wave function into the Schrodinger equation with the free electron mass and lattice potential.
2. For electron near the band edge, treat the $k \cdot p$ term in the Hamiltonian operator as a perturbation.
3. Provided the band energy $E$ ($k=0$) and wave function is known, expand the generalized wave function in terms of those at $k=0$, and solve the resulting Hamiltonian.

For our purposes, the Hamiltonian is extended to include the effect of spin orbit coupling:

$$\left( \frac{p^2}{2m} + \frac{\hbar k \cdot p}{m} + \frac{\hbar^2 k^2}{2m} + V(r) + \frac{\hbar}{2} (r \times p) \cdot \sigma \right) \phi_{nk} = E_{nk} \phi_{nk}$$

Where $\lambda$ is the strength of the spin-orbit coupling. The expression for the Hamiltonian after diagonalization [73] is:

$$\mathcal{H} = \begin{bmatrix} P + Q & -\sqrt{3}R & -i\sqrt{3}/2S \\ -\sqrt{3}R & P + Q + 2/3\Delta & i\sqrt{3}/2S - \sqrt{2}/3\Delta \\ -i\sqrt{3}/2S & -i\sqrt{3}/2S - \sqrt{2}/3\Delta & P - 2Q + \Delta/3 \end{bmatrix}$$

Where:

$$P = \left( \frac{\hbar^2}{2m} \right) \gamma_1 (k_x^2 + k_y^2 + k_z^2)$$
Q = \left( \frac{\hbar^2}{2m} \right) \gamma_2 \left( k_x^2 + k_y^2 - 2k_z^2 \right)

R = \left( \frac{\hbar^2}{2m} \right) \sqrt{3} \left[ -\gamma_2 (k_x^2 - k_y^2) + 2t\gamma_3 k_x k_y \right]

S = \left( \frac{\hbar^2}{2m} \right) 2\sqrt{3} \gamma_3 (k_x - ik_y) k_z

\Delta = \text{spin-orbit splitting energy}

\gamma_1, \gamma_2, \gamma_3 \text{ are Luttinger-Kohn parameters of the semiconductor.}

![Figure 3.7 Schematic of Band Structure showing relevant energy bands](image)

To summarize, we know the essential band gap of a GaAs$_{1-x}$N$_x$ system via the BAC model where the conduction band is assumed to change following equation (3.4). Experimentally derived parameters such as the Luttinger Kohn parameters and spin orbit splitting energy are utilized to obtain the band structure of the system in the vicinity of $k = 0$. 
3.3.2  **Effect of Lattice mismatch on the Band Structure**

GaAsN/GaAs is a highly strained system, due to the large lattice mismatch caused by the introduction of nitrogen. The lattice constant shrinks, leading to a biaxial tensile strain on the GaAsN layer.

![Lattice mismatch diagram](image)

**Figure 3.8** Variation of lattice constant shown schematically, highlighting the tensile strain along the horizontal plane.

Any effect of strain as in this case, with growth in (001) direction and a resulting biaxial strain can be expressed as the sum of three components:
This is the sum of hydrostatic, tetragonal and trigonal matrices of deformation, respectively. In case of growth along (001) direction, the off diagonal components can be taken to be zero, and the resultant is the sum of hydrostatic and tetragonal contributions only. Hydrostatic strain shifts down the position of the valence band, while the tetragonal (biaxial) strain splits the degeneracy of the valence bands. The effect on the \( m_j = \pm \frac{1}{2} \) level (also called light hole LH) is to get shifted higher up in energy while the effect on \( m_j = \pm \frac{3}{2} \) (also called heavy hole HH) is to get shifted to lower energy. The reciprocal of the curvature of an energy band referring to the \( E=E(k) \) curves in Fig 3.7 is essentially the effective mass of the carriers occupying it. The curvature of the LH band (which shifts to a lower energy under tensile strain), is affected such that \textit{light holes become heavier than heavy holes}. Hence, if the hydrostatic deformation potential for the crystal is \( a_v \) and the tetragonal potential is \( b \), the effective shifts are respectively:

\[
-\mathbf{P}_k = a_v(e_{xx} + e_{yy} + e_{zz})
\]
\[ \delta E_{3/2} = -Q_e = \frac{b}{2}(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}) \quad \text{(3.11)} \]

\[ \delta E_{1/2} = \frac{Q_e - \Delta}{2} + \frac{1}{2} \left( \sqrt{9Q_e^2 + \Delta^2 + 2Q_e\Delta} \right) \quad \text{(3.12)} \]

Hence the Hamiltonian from eq. 3.8 becomes:

\[ \mathcal{H} = \begin{bmatrix}
P + Q - P_e - Q_e & -\sqrt{3}R & -i\sqrt{3/2}S \\
-\sqrt{3}R & P + Q + \frac{2}{3\Delta} - P_e - Q_e & i\sqrt{3/2}S - \sqrt{2/3}\Delta \\
-i\sqrt{3/2}S & -i\sqrt{3/2}S - \sqrt{2/3}\Delta & P - 2Q + \frac{\Delta}{3} - P_e - Q_e
\end{bmatrix} \quad \text{(3.13)} \]

And the separation between the subbands:

\[ \delta E = \delta E_{1/2} - \delta E_{3/2} = \frac{3Q_e - \Delta}{2} + \frac{1}{2} \left( \sqrt{9Q_e^2 + \Delta^2 + 2Q_e\Delta} \right) \quad \text{(3.14)} \]

The schematic of the band diagram would now be in this form (Fig.3.9).
Figure 3.9 Schematic of Band Structure showing relevant energy bands shifted due to biaxial strain. As can be noticed, the band gap has reduced slightly.

3.3.3 Extracting Confinement Energy by the Transfer Matrix Method

Once the valence and conduction band energy levels for both GaAsN and GaAs are determined, they can now be used to evaluate the value of energy levels in a multi-quantum well system, which is equivalent to an extended “particle-in-a-box” system of elementary quantum mechanics. The solutions are obtained by determining two continuity conditions for the wave function $\varphi$ at the boundary of interlayer $i$ and $i+1$:

$$
\varphi_i = \varphi_{i+1}, \quad \text{and} \quad \left| \frac{1}{m_{\text{eff}}^i} \frac{\partial \varphi_i}{\partial z} \right|_{z=z_i} = \left| \frac{1}{m_{\text{eff}}^{i+1}} \frac{\partial \varphi_i}{\partial z} \right|_{z=z_{i+1}}
$$

3.15
Figure 3.10 Schematic of the regions for which the solutions are obtained with I(GaAs) and II(GaAsN). P and D denote the region of interest for propagation and interface solution matrices respectively.

These are the boundary conditions for dissimilar interfaces [74]. The transfer matrix can now be found between the $i^{th}$ and the $i+1^{th}$ layers to relate the complex coefficients of the wave functions within them. Hence, the solution of the system consists of two components: the propagation solution within a layer, and the change that occurs at an interface boundary. The interface change is given by:

$$
\begin{bmatrix}
A_i \\
B_i
\end{bmatrix} = 
\begin{bmatrix}
1 + \frac{m_{eff}^i k_{i+1}}{m_{eff}^{i+1} k_i} & 1 - \frac{m_{eff}^i k_{i+1}}{m_{eff}^{i+1} k_i} \\
1 - \frac{m_{eff}^i k_{i+1}}{m_{eff}^{i+1} k_i} & 1 + \frac{m_{eff}^i k_{i+1}}{m_{eff}^{i+1} k_i}
\end{bmatrix}
\begin{bmatrix}
A_{i+1} \\
B_{i+1}
\end{bmatrix} = D_i \begin{bmatrix}
A_{i+1} \\
B_{i+1}
\end{bmatrix}
$$

Where $k_i$ refers to the wave vector in the $i^{th}$ layer. The propagation within a layer of thickness $t$ is given by:
Hence for a series of \( N \) layers, the total transfer matrix is given by:

\[
\begin{bmatrix}
A_i \\
B_i
\end{bmatrix}
= 
\begin{bmatrix}
e^{-ik_{i+1}t_{i+1}} & 0 \\
0 & e^{ik_{i+1}t_{i+1}}
\end{bmatrix}
\begin{bmatrix}
A_{i+1} \\
B_{i+1}
\end{bmatrix}
= P_i
\begin{bmatrix}
A_{i+1} \\
B_{i+1}
\end{bmatrix}
\]

\[3.17\]

The physical requirement of decay of the solution far from the boundaries can then be used to obtain the confinement energy. For a GaAs system with barrier = 15 nm \( \text{GaAs}_{0.97}\text{N}_{0.03} \) quantum well thickness of 6 nm, energy levels energies of the valence ELH and EHH levels and the electronic energy levels have been calculated using the above method (Fig. 3.11).

Figure 3.11 Variation of the energy of electrons and holes as a function of nitrogen for \( \text{GaAsN}(6 \text{ nm})/\text{GaAs}(15 \text{ nm}) \) QW system
3.4 Absorption Coefficient for a Multi-Quantum Well System

Calculation of the energy levels helps determine the transition energy from the holes to the electrons, and hence the absorption properties. The absorption coefficient $\alpha$ is the probability of absorption of a photon per unit length, expressed in units of cm$^{-1}$ or m$^{-1}$. If $n_p$ is the number of photons falling onto a material along $z$ direction with a thickness $z$:

$$n_p(z) = n_p(0)e^{-\alpha z} \quad (3.19)$$

Typical values of absorption coefficient for a direct band gap system like GaAs is about $10^4$ cm$^{-1}$. The sequence of absorption is quite vital to determine the overall absorption of a system as the loss due to the preceding layers must be taken into account (Fig. 3.12).

![Absorption of photon flux $\Phi$ through a series of $n$ quantum wells of thickness $t_{QW}$ and an intrinsic (barrier) region of thickness $t_{int}$.]  

To calculate this, we require the rate of transition as well as the energy absorbed by every transition. If the electron absorbs a photon and transitions from $|a\rangle$ to $|b\rangle$, then according to Fermi's Golden Rule (see Section 2.2.5) the transition rate is given by:

60
When we combine this expression with the value for incoming flux and its geometry, we obtain:

\[ \alpha(h\omega) = \frac{4\pi^2 e^2}{n_r c \epsilon_0 m_0^2 \omega \Omega} \sum \sum |\epsilon \cdot p_{ba}|^2 \delta(E_b - E_a - h\omega)(f_a - f_b) \]  

Where \( \alpha \) is the strength of the absorption, \( \epsilon \cdot p_{ba} \) is the momentum matrix element between bands b and a, whose square modulus is referred to as the “oscillator strength”, \( m_0 \) refers to the effective mass of the charge carrier, \( \omega \) is the angular frequency of the incoming radiation, \( n_r \) is the refractive index of the solar cell material, \( \Omega \) is the solid angle from which the sunlight is received, and \( f_a \) refers to the Fermi-Dirac distribution function, or the probability that the state a is occupied. At absolute zero, this function becomes the same as the Heaviside function.

\[ |f_a|_{T=0} = \frac{1}{1 + e^{E_a - E_F/k_B T}} \]  

Evaluating these expressions, the absorption coefficient for the bulk, quantum well, as well as the excitonic absorption is calculated [75]–[77]:

\[ \alpha(\text{bulk}) = \frac{2\pi^2 e^2 |\epsilon \cdot p_{ba}|^2}{n_r c \epsilon_0 m_0^2 \omega} \left(\frac{2\mu}{\hbar}\right)^2 \left(\frac{E - E_g}{\hbar}\right)^2 \]  

\[ \alpha(\text{QW}) = \frac{4\pi^3 e^2 |\epsilon \cdot p_{ba}|^2}{n_r c \epsilon_0 m_0^2 \omega L} \left(\frac{\mu}{\hbar}\right) \sum_{k} \Theta \left(\frac{E - E_g - k^2 \pi^2 \hbar^2}{2\mu L^2}\right) \]
Figure 3.13 Calculated absorption coefficient of GaAsN single quantum well showing the improvement in absorption in (i) bulk GaAs, (ii) GaAs$_{0.966}$N$_{0.034}$ Quantum Well without thermal broadening, and (iii) excitonic absorption and (iv) the overall performance of the QW at 300K with well width of 6 nm.

3.4.1 Effect of the Electric Field Strength

The oscillator strength of the absorption is dependent on the matrix element connecting two states, i.e. it is determined by the overlap of the wave functions of the respective states. In a quantum well, the wave function corresponding to each energy level is either odd or even, and this factor contributes to the selection rules between two states. For example, for heavy and light hole wave functions, their corresponding convolution with the electronic states decides whether a transition can occur or not, as shown in Fig. 3.14.
Figure 3.14 Schematic [78] of wave functions for (a) Heavy hole ($m_j=3/2$) and (b) Light hole ($m_j=1/2$) energy levels showing the forbidden transition from $m=2$ to $n=1$.

Figure 3.15 Schematic of wave functions without and with an electric field, showing the breaking of selection rule.

In addition to the selection rules themselves, another factor that can affect the wave function overlap is the electric field. It can be seen for instance, that in the presence of an electric field, the wave function symmetry is broken in the direction of the field, hence allowing transitions to occur that would normally be forbidden. Since the oscillator strength depends on the electric field, we can evaluate this dependence from the matrix element $|e \cdot p_{ba}|^2$ which is the modulus of the wave-function overlap. Fig. 3.15 shows a schematic of the process, while Fig. 3.16 obtains the variation of the electronic wave
function as a function of increasing electric field from 0 to 100kV/cm. Typical values of electric field in a depletion region are of the order of 40-50 kV/cm.

Figure 3.16 Dependence of Ee1 and Ehh2 energy level wavefunctions on the applied electric field, within a 6 nm GaAsN (3.4%) QW/ 15 nm GaAs, showing the oppositely directed shifts.

It can be seen that the wave function for Ehh2 transitions from a perfectly anti-symmetric sine wave to (roughly) a displaced Gaussian, which is obtained by including the contribution $E \cdot x$ to the potential of the Hamiltonian, where $E$ is the electric field. The overlap of the two wave functions (oscillator strength) can be calculated by:

$$|\varepsilon \cdot \mathbf{p}_{ba}|^2 = |\langle \varphi_n | \varphi_m \rangle|^2$$

3.26

Where $\varphi_n$ and $\varphi_m$ are the $n^{th}$ and $m^{th}$ energy level wave function respectively. Calculation
of the oscillator strength yields a steady decrease as a function of well width as well as electric field strength, as shown in Fig. 3.17.

Figure 3.17 Dependence of oscillator strength of a 1 eV (Ehh1-Ee1) transition on well width and the strength of the electric field. The low strength for width <1nm indicates incomplete confinement, while the low strength at higher electric fields is due to asymmetry in the wave function.

Including the effect of electric field, the absorption coefficient was calculated for previously grown dilute nitride MQW solar cell [8].

3.4.2 Quantum efficiency of Dilute Nitride MQW solar cell

Using the absorption coefficient of a single quantum well in a specific configuration (decided by the number of wells, barrier thickness, doping densities etc.), one can model the current generated in a solar cell due to that absorption. In most cases it is seen that
due to the presence of an electric field in the intrinsic region, carrier escape is close to 100% [79]. This factor, called internal quantum efficiency, assumes that every electron-hole pair created due to light absorption is separated and contributes to the current (see Section 2.3.1). Calculation of the spectral response involves the calculation of the current contributed by p, i, and n regions of the solar cell, coupled with the extraction from QW region. If $\alpha_b$ is the absorption coefficient of the barrier and $\alpha_{QW}$ that of the wells, the current generated from the intrinsic region is given by [80][81]:

$$J_i = q(1 - R)\Phi e^{-\alpha_b X_p}(1 - e^{-\alpha_b(X_i + N X_{QW})})$$  

$$J_{QW} = q(1 - R)\Phi n^N \left[ \frac{\alpha_{QW} L_e}{\alpha_{QW} L_e - 1} \left( e^{\frac{X_p}{L_e}} - e^{\frac{\alpha_{QW} X_p}{L_e}} \right) \right.$$

$$+ \left. \frac{\alpha_{QW} L_h}{\alpha_{QW} L_h + 1} \left( e^{\frac{X_i}{L_h}} - e^{\left(\frac{\alpha_{QW} + 1}{L_h}X_i\right)} \right) \right]$$

Where,

$\Phi$ is the spectral photon flux,

$R$ is the loss due to reflection,

$n$ is the extraction efficiency,

$N$ is the number of QW,

$L_e$ and $L_h$ are electron and hole diffusion lengths,

$X_i$ and $X_p$ are intrinsic and p-region thicknesses.
Figure 3.18: Spectral response calculated for a typical 15-period 6nm GaAsN QW/15 nm GaAs barrier system with contributions from p-, i-, n- and QW-regions.

It is seen that the addition of intrinsic layer with QW accounts for significant below-band-gap absorption, as expected. Experimental results of the external quantum efficiency (so called due to dependence on external contacts and device parameters) as well as I-V characteristics on previously-grown MQW solar cells were now modeled with this method (grown via chemical beam epitaxy or CBE). Carrier extraction efficiency factor is $n = 1$, implying full carrier escape was assumed for all QW’s, to evaluate I-V characteristics, which showed that current extraction was ~40% of what was expected (Fig. 3.19). Hence, utilizing $n = 0.41$, the quantum efficiency was fit to the experimental data as shown in Fig. 3.20.
Figure 3.19 Comparison of IV characteristics of a 15-period GaAs\textsubscript{0.981}N\textsubscript{0.018}/GaAs MQW solar cell with theoretical model assuming 100% carrier extraction efficiency (n=1).

Figure 3.20 Comparison between experimental data and theoretical simulation of MQW absorption in a 15 period GaAs\textsubscript{0.981}N\textsubscript{0.018}/GaAs, showing a reasonably good fit only when QE was assumed to be ~40% of its assumed value.
Both I-V and EQE results hence required a modification of the assumption of full carrier escape, and the escape efficiency $n = 0.41$. A possible reason for this reduction could be due to the presence of defects in the GaAs barrier, generated by the presence of nitrogen. It can be seen from Fig. 3.20 that there is a drop in absorption (EQE) just below 1.4 eV, and this fact also supports incomplete carrier extraction, possibly due to contamination of GaAs barrier. A disadvantage of CBE-growth is the presence of hydrogen in the CBE chamber that serves to degrade the quality of growth [82]. This requires the development of MBE growth of high quality sharp interface QW’s, a topic that will be covered in the Chapter 4. A method to overcome carrier extraction issues would then be discussed in Chapter 5.
Chapter 4: Growths of Dilute Nitrides by Molecular Beam Epitaxy

4.1 Introduction

Due to the large difference of chemical characteristics between nitrogen and arsenic, the equilibrium solubility of nitrogen in GaAs is very small. As a result, attempts at growth of dilute nitrides primarily involve techniques where growth takes place far from thermodynamic equilibrium, like use of metal organic chemical vapor deposition (MOCVD), also referred to as atmospheric-pressure metallic-organic vapor phase epitaxy (MOVPE) [3], [58], molecular beam epitaxy (MBE, which uses solid sources) or chemical beam epitaxy (CBE, which uses metalorganic sources). Compositional control and uniformity of dilute nitrides is easier to achieve with MBE [83]–[86] or CBE [87]. In addition, since dilute nitride properties are detrimentally affect by the presence of H\textsubscript{2} in the system [88], which is generally present as the metal-organic carrier gas in the operation of CBE, MBE seems more suitable to grow dilute nitrides. Various sources for nitrogen have been used in literature, including DC (direct current) and RF (radio frequency) plasma sources, dimethylhydrazine, ammonia, etc. [52]. In this work, an RF Plasma source was used. The following sections will describe the growth process as well as the plasma source optimization necessary to obtain high quality growth of GaAsN/GaAs quantum wells.
4.2 Preliminary Investigations of Dilute Nitride Growth

4.2.1 MBE Operation

Growth of a single-crystal semiconductor film on a single crystal substrate is done by “epitaxial” growth derived from the Greek word ἐπί-τάξις (“arranged upon”). For the growth of lattice matched solar cells, epitaxial techniques are ideal, and there are many ways epitaxial growth techniques that are used nowadays. The focus here would be epitaxy in ultra-high-vacuum (UHV), in particular, molecular beam epitaxy, a technique that was pioneered by the John Arthur and others in the late 1960’s [89]–[91].

UHV enabled epitaxial growths enable precise control of the beam fluxes and the growth conditions due to the ultra-high vacuum conditions ($10^{-8}$-$10^{-9}$ Torr) maintained inside the growth chamber. This results in a long mean-free path (the average distance traversed by the gas molecule between successive collisions) in the chamber, justifying the name “beam”.

In MBE atomic beams (Be, Si, Al, Ga, and In) and molecular beam As$_4$ (cracked at high temperature to As$_2$) are delivered from standard Knudsen effusion cells. The relative composition and doping levels of the layers are controlled by the evaporation rates of the elements and dopants. Traditionally, simple mechanical shutters in front of the beam sources are used to interrupt the beam fluxes, enabling atomic scale control.
Most ternary and quaternary semiconductors (e.g. AlGaAs, GaAsP) have complete miscibility across the entire alloy range, and can hence be grown using standard effusion cells. Nitrogen ($\text{N}_2$), however is extremely stable with an energy of dissociation 9.76 eV [92], has a large miscibility gap [93], and fails to incorporate into the surface, thus requiring the formation of N atomic species. However the dissociation energy is much higher as compared to 3.96 eV for arsenic and 5.03 eV for phosphorus which use standard UHV cracking methods to generate active species. The most successful method of obtaining reactive atomic N has been the use of an RF-plasma source.
4.2.2 *Nitrogen Plasma Source Operation*

The nitrogen RF plasma source, so named due to radio-frequency (RF) generation of plasma, generates an intense beam of high energy nitrogen atoms, molecules and ions. The plasma is controlled via the tunable RF coil matching network while high-purity nitrogen is fed into the system. An EPI-Uni-BulbTM RF Plasma source operating at 13.56 MHz provides the active (atomic) N species through an end plate with 25 holes of 0.203 mm diameter. In standard operation, a steady yet high flux of nitrogen, of up to 3 standard cm$^3$ (sccm) is supplied to the plasma source when it is open to the chamber, and after a period of stabilization of 6 minutes (dependent on the system), power is supplied to the RF coil and the plasma is fired up. Powers of up to 600 W can be reached by the power supply of the coil. Following this, nitrogen flow is reduced to about 1 sccm, and the plasma source is now ready for operation. Typical values during growth range from 300-550 W, 0.2-2 sccm. A schematic of the plasma source is shown in figure 4.2.

![Figure 4.2 Schematic of a typical plasma source showing the RF induction coil and the exterior](image-url)
matching network which must be tuned to generate a steady plasma.

It is of interest to us to study the species generated in the chamber, as observed by the spectra of the N-plasma, obtained by an Ocean Optics™ USB 4000 spectrometer and analyzed by OOIBase32 Software. The bands below 700 nm are known to be associated with the atomic transition in N species [94], while those above 700 nm are associated with the molecular transitions of the same (Fig 4.3). Since it is necessary to obtain a high amount of atomic N, the atomic to molecular ratio has to be determined. This can be done by comparing the ratio of integrated intensity from the peaks at 745, 821 and 869 nm, to that of the peaks at 550, 580 and 650 nm [84], and is seen to depend directly with plasma power.

![Figure 4.3 Spectrum of N plasma showing the peak of atomic N at ~745 nm, among other transitions, above 700 nm, while molecular N₂ (500-700 nm) and ionic N₂⁺ (300-400 nm, not shown here) give higher frequency response. Comparison between high and low power is seen, showing increase in atomic species with power.](image)
Traditionally, the N plasma is fired just before the start of dilute nitride growth, with the manual shutter closed. A period of stabilization follows the firing, which generally lasts between 20s-360s, depending on the RF power and nitrogen flow rate. Once the flow is stabilized to the desired value, the manual shutter is opened and N-incorporation is initiated. To avoid an excessive nitridation of the GaAs surface (replacement of As by N), the growth of dilute nitrides is initiated by insuring the simultaneous arrival of Ga and As flux at the surface. Growth interruption is necessary in order to change the substrate temperature and to reduce the surface nitridation. The manual shutter is not an effective means of preventing the N species from interacting with the sample, as seen from the N flux measurements from the RGA Mass Spectrometer, and shown schematically in Fig. 4.4. Hence, some earlier attempts to improve crystal quality have used closed shutter configuration during growth [95].

Nitrogen plasma source requires up to two hours of cooling time, before re-starting, hence this setup for the growth of sharp interface quantum wells requires one to grow continuously without plasma re-firing. This causes growth of dilute nitride with a smaller composition even when the shutter is closed for the required GaAs. It is important to characterize the nature of interface formation under these conditions (hereafter known as “the conventional plasma settings”), to determine their feasibility for the required dilute-nitride structures, particularly the interface sharpness of quantum wells.
Figure 4.4 Schematic of conventional N Plasma source showing flux control achieved with the manual shutter open (a) and closed (b), showing the persistence of nitrogen flux even in the closed position due to internal reflections from the back of the shutter.

4.3 Growth kinetics

Growth kinetics of dilute nitride III-V semiconductors is different from that of traditional arsenides, phosphides, or antimonides, as there is no dependence of N incorporation on group –V species. On the contrary, under constant plasma conditions, nitrogen concentration in MBE has been known to depend inversely on group-III growth rate [83] [96]. The inverse linear dependence is due to the complete adsorption of incident N onto GaAs growth surface, i.e., N has unity-sticking coefficient to GaAs.
It has been shown earlier in this laboratory [82] as well as in other studies [97] that the effect of increase in plasma intensity leads to increase in N-incorporation. This was seen to be true in this work as shown in Fig. 4.6 (determination of nitrogen concentration by X-ray diffraction will be discussed in the section 4.4.1). It has also been observed that increasing the flow rate also significantly increases the incorporation of nitrogen, particularly due to the presence of high-energy species [98][99][100]. Presence of high-energy ionic species ($N_2^+$ and others), which becomes prevalent at higher plasma power, degrades the quality of dilute nitrides [101][102].
Growth temperature affects growth of dilute nitrides in two major ways. Firstly, incorporation of nitrogen decreases with increasing temperature, as seen in the literature [103] as well as this study. Secondly, growth below substrate temperatures of 450 °C is increasingly difficult, leading to a large number of point defects that can be recovered via annealing [104].

Considering these factors, growth of dilute nitrides in MBE have been done with growth temperature in the range 440-460 °C, with the GaAs layer being grown at the usual value of 580 °C, and a plasma flow rate of 1sccm, unless otherwise stated.

4.4 GaAsN/ GaAs interface characterization

To determine the nature of the GaAsN, three samples were used. The first sample (sample A) described here was previously grown in the Riber 32 Chemical Beam Epitaxy system.
while samples B and C were grown in the Riber 32 MBE system. The dilute nitride (GaAsN) was grown on GaAs (001) substrates, consisting of a ~100-nm layer of GaAsN (grown at 460 °C) over GaAs buffer (grown at 600 °C). The Ga and As flux were in keeping with a 1 monolayer/s growth rate, and the N flow was maintained at 1 sccm for all samples.

4.4.1 High Resolution X-ray Diffraction (HRXRD)

High resolution X-ray diffraction (HRXRD) is an excellent non-destructive way to analyze structures with epilayers. In general, XRD is used to analyze not only the quality of the epilayers grown but many other important structural characteristics such as lattice constant, lattice mismatch and resulting strain, alloy composition, epilayer thickness, periodicity of superlattices, lattice relaxation, defect density etc. When an epilayer is grown on a substrate, depending on the type of the layer grown the XRD spectra may yield two or more peaks. There will be a main peak from the substrate at the Bragg angle we expect for the particular material system (typically the substrate) and another peak for the epilayer itself at a different angle from the substrate.
Figure 4.7: Three examples of HRXRD analysis on as grown GaAsN/GaAs samples. Sample S1 is fully relaxed, while sample S2 has both a misorientation (as indicated by the split peak) as well as some relaxation. Sample S3 gives the best results: it is 3.67% GaAsN (96 nm)

The relationship between strain and the shift in angle is easily determined by differentiating the Bragg relation:

\[ n\lambda = d\sin\theta \rightarrow d = \frac{n\lambda}{\sin\theta} \rightarrow \frac{\delta d}{d} = -\cot\theta d\theta \]

Hence strain, \( \frac{\delta d}{d} \), is a function of the separation \( d\theta \). If strain is negative (if the epilayer is smaller than the substrate), the shift is positive, and vice versa, while relaxation reduces the shift magnitude, bringing it closer to the substrate peak.

We can evaluate the strain, and hence the composition, for strained layer by taking into account the Poisson Coefficient:
Similarly, the fringes that appear on either side of the main peak can be attributed to the interference caused by the film thickness. For orders \( n_1 \) and \( n_2 \) of fringes on either side of the peak, from Eq. 4.1 we have the film thickness:

\[
t = \frac{\lambda \ast (n_1 - n_2)}{2 \sin(\theta_1) - \sin(\theta_2)}
\]

Finally, the full-width-at-half-maximum (FWHM) gives an estimate of the presence of defects in the crystal, as a highly dislocated sample (e.g., where GaAsN has relaxed atop GaAs leading to mismatched growth in the QW regime) gives a large broadening of the peak. This method was used to determine the nitrogen plasma growth conditions for obtaining \( \sim 3\% \) N in order to design the 1eV solar cell. Bede 200\textsuperscript{TM} high resolution diffractometer was used for all characterizations.

### 4.4.2 Photoluminescence (PL) and Transmission Electron Microscopy (TEM)

Photoluminescence (PL) results are shown in Fig. 4.8 from a GaAs_{0.97}N_{0.03} sample A which had undergone rapid thermal processing (800 °C for 30s). In addition to the high-intensity peak of GaAs and the GaAsN peak, there is a contribution at about 1.36 eV, which has previously been attributed to N accumulation at the GaAsN/GaAs interface based on PL and TEM analysis [105][106]. The peaks obtained from the GaAsN layer
correspond to the $E_{\pm 3/2}$ and $E_{\pm 1/2}$ transitions, and comparison with the N composition dependence suggests that the contribution around 1.34 eV can be attributed to lower N-composition (0.8%N) in the parasitic layer. The values of the energy levels have been calculated as described in Chapter 3.

The samples were also examined using high-angle annular dark-field (HAADF) imaging in a JEOL-2010F high-resolution scanning transmission electron microscope (STEM) operated at 200-keV, which provides a nominal probe size of ~2 Å. The lighter color in contrast to the darker background in HAADF STEM images reveals the presence of N-interstitials at the interfaces of the GaAsN/GaAs layers, suggesting the presence of interstitial N. This is seen most clearly for sample A, as shown in Fig. 4.9. The image contrast of the GaAsN is mostly uniform throughout the layer, indicating that the quality of the interface had no reason to deteriorate, thus helping to isolate the effect of N flux on the sample.
Figure 4.8 Integrated Photoluminescence (log scale) of GaAsN (3%, 100 nm)/GaAs sample (for 1.05 eV band gap), grown with conventional plasma source operation with shutter closed during plasma firing, showing strong band-edge luminescence of GaAs$_{0.97}$N$_{0.03}$, as well as luminescence associated with a parasitic layer with low-N%. Exciton peaks ($E_{3/2}$ and $E_{1/2}$) are compared to the expected values of energy as a function of N composition, giving a range 0.8±0.02% for the parasitic layer.
Figure 4.9 Medium magnification HAADF-STEM showing GaAsN(3.0%)/GaAs interface discontinuity at two positions and the schematic of growth sequence for conventional design. Shade brightness in the micrograph is tentatively ascribed to presence of N-interstitials. It should be noted that despite a closed shutter parasitic spike in nitrogen concentration due to the firing of the plasma is clearly seen.

This shows that it is very important to curtail the excess nitrogen, by some method.

4.5 Run-vent System Installation

4.5.1 Design of Run-Vent System

With the requirement of reducing the N-flow accumulation behind the shutter of the N-plasma source, a run-vent system was designed and implemented as shown. A pneumatic gate-valve is introduced between the plasma source and the chamber, with a VCR-connected pneumatic valve installed in the line leading out of the gate valve itself. The two pneumatic valves are out of phase, i.e., when the gate valve is closed, the pneumatic valve is open and vice versa. During standard conditions, as the system is isolated from
the plasma source, the gate valve is normally closed while the pneumatic valve is
normally open. The switching was controlled manually in this work, but could be
converted into an automatic operation. The flow of nitrogen is directed to the vent turbo
via the tubing and a leak valve, creating suction of any accumulated N behind the gate
valve. This geometry ensures that even when the N Plasma is not exposed to the low
pressure of the MBE chamber, evacuation is not stopped.

The modified system is shown in Figs. 4.10 and 4.11. The presence of this system was
expected to create a reduction in the overshoot, and a steady plasma can continue to
operate without any need of its re-firing. The overshoot and stabilizing of the N plasma
flux before and after leak valve optimization of the run-vent system was studied using the
RGA Mass Spectrometer, as shown in Fig. 4.12. The overshoot after the opening of the
gate valve requires just about 3s to reduce to its nominal value, and a similar time is
required for the removal of nitrogen upon the closing of the gate valve. This time frame
ensures a minimal variation of the nitrogen composition with the gate valve operation.
The opening and closing of the Ga shutter can be optimized by varying the leak-valve
openings to offset the limited overshoot actually observed, resulting in an overall sharp
transition and uniform composition during growth.
Figure 4.10: Detailed schematic of modified run-vent system showing the system specifications. Leak valve and leak valve 2 control the vent-rate, which are optimized to obtain sharp nitrogen transients upon opening the gate valve. The pneumatic-valve and the gate valve are linked electrically, such that one opens when the other closes.

Figure 4.11 Schematic of operation sequence of the modified run-vent system, with the addition of a Normally Open (N.O.) pneumatic valve at the back of a Normally Closed (N.C.) gate valve
4.5.2 Growth of MQW via Run-Vent System

To verify interface quality, two GaAs$_{0.979}$N$_{0.021}$ multiple-quantum well samples (B and C) were grown with 4 periods of QWs with width 4nm and 6 nm, separated by a barrier of 12 nm. Reflection High Energy Electron Diffraction (RHEED) was monitored in-situ during growth. Prior to the installation of the run-vent system, the growth of the QWs (in sample B) involved a growth interruption of 25s while the N plasma was fired and stabilized, which caused the formation of 3D growth pattern (indicated by spots on the RHEED screen) at the start of the N plasma growth, with the 2x4 pattern getting converted to 2x1 in the [1 -1 0] direction, with subsequent partial recovery of the striped pattern with growth of the GaAs layers. After the modification to the setup, this growth was repeated with sample C. In this sequence of operation, the plasma was fired before
the start of the QW growth, with the gate valve closed. At the start of the QW growth, gallium was closed in the beginning for 5 sec only, in order to simultaneously open the gallium shutter and the N plasma gate valve to grow the first QW. Subsequent MQW growth was done without growth interruptions, and only via the switch operation. This showed a clear 2x4 RHEED pattern throughout growth of the MQW sample, especially at the interface, and also gave a sharp interface as seen via HAADF-STEM (Fig. 4.13).

Figure 4.13 HAADF-STEM images of Sample C showing the formation of clear 6 nm GaAsN (2.1%) QW.

The RHEED results from the two samples during growth of quantum wells are shown in Fig. 4.14. The nitridation of the surface is the likely cause of the loss of quality of the interface in sample B, giving a spotty pattern, while sample C showed clear streaks throughout growth.
Figure 4.14: RHEED pattern of GaAs\textsubscript{0.979}N\textsubscript{0.021} QW samples recorded at the onset of GaAsN growth following a 20 sec interruption of the GaAs barriers (a) conventional shutter activated operation, with growth interruption prior to start of GaAsN growth (Sample B), by (b) gate valve operated run-vent system without growth interruptions. (Sample C)

4.6 Rapid Thermal Annealing (RTA) Characterization

Annealing behavior in dilute nitrides is known to be unique compared to all similar dilute nitride alloys: there is a dramatic increase (30-75x) in PL efficiency [107][108]. In particular, low temperature growths used to incorporate high quantities of nitrogen are subjected to RTA [104]. Annealing was optimized in this lab for a series of GaAsN/GaAs samples as shown in Fig.4.15.

Figure 4.15 Change in below band-gap PL intensity of GaAs\textsubscript{0.969}N\textsubscript{0.031}(80nm)/GaAs sample for different temperatures showing optimal response at 830 °C for 30 s. Nearly 2 orders of magnitude improvement is observed (courtesy MC Wu, unpublished).
RTA conditions were optimized for samples 1 and 2. Instead of an improvement, a significant degradation in PL intensity is observed after RTA at 800 °C for 30 sec (see Fig. 4.16). This is most likely due to diffusion of nitrogen into the barrier layers of the QW, which creates defects within the barrier. In order to verify this, HAADF-STEM results for the sample before and after RTA was analyzed, as shown in Figure 4.17.

Figure 4.16 Degradation of PL at 10K for Sample 1 following RTA @ 800 °C for 30 s. A shift of 40 meV is observed in the GaAs peak, possibly due to incorporation of N into the barrier region.
4.7 Summary

We have studied the process used to grow dilute nitrides, and described the nitrogen plasma source operation and its limitations for growth of sharp interface quantum wells. Characterization of samples grown with the conventional plasma setup clearly showed a degradation of the interface, making an alternative approach necessary. This approach was taken with the help of an improved gate-valve operated run-vent design for nitrogen, generating sharp transients and high quality interfaces as shown by HAADF-STEM. Samples with MQW structure were grown with and without this modification. With the run-vent design, the RHEED remained 2D throughout the growth, including at the interfaces, and the surface quality was very good. These results suggest that the run-vent system shows promise for developing high quality QW structures, which are essential for designing resonant-tunneling GaAsN MQW systems that will be examined in the next
chapter. Optimized rapid thermal annealing of MQW samples showed degradation of interface quality, as compared to as-grown samples.
Chapter 5: Development of Symmetric and Asymmetric MQW Solar Cell for Improved Carrier Extraction

5.1 Introduction

Following the development of sharp quantum well interfaces as well as the modeling tools required to simulate a p-i-n MQW GaAsN solar cell, prior to designing an improved solar cell it is necessary to obtain the state-of-the-art results on the development of dilute nitrides, both with and without quantum wells for photovoltaic applications. A description of an improved design would then be discussed.

5.2 State of the Art: Dilute Nitride Solar Cells

Following the proposal of dilute nitrides as a candidate for multi-junction solar cell [4] there was an increase in activity devoted to produce a suitable GaAsN sub-cell [7], [109][110]. The first observation of reduction of diffusion coefficient in dilute nitrides [109] showed that for a wide range of samples, the upper bound for the diffusion length was given by the depletion width of the cell. Characterization of diffusion lengths also proved difficult due to type conversion from p to n-type seen upon post-growth annealing [111]. Lifetime measurements over the whole composition range of N in both bulk [64] and QW devices [63] showed a short carrier lifetime restricted to 0.2-1 ns, a factor of 10 to 100 lower than GaAs for comparably doped material. Mobility of electrons were
observed to reduce much faster as a function of $[N]$ as compared to holes [5][6], suggesting a greater need to improve electron extraction.

Study of recombination revealed that as compared to an ideality factor ($n$) of 1 that is obtained in case of recombination by diffused carriers, ideality factors for GaInNaAs p–n junctions have shown values of 1.2-1.5. In addition, the magnitude of GaInNAs junction dark current was orders of magnitude greater than expected by diffusion recombination [112], suggesting the presence of trap-states in the band-gap.

With regard to current extraction, current collected from p-type region of GaInNAs has been observed to correlate with the depletion width of the cell, and the highest GaInNAs photocurrents reported to date have been for wide-depletion-width GaInNAs grown by MBE [113][114]. This suggests the use of p-i-n structures to enhance current response of the cell. In addition to post-growth annealing already mentioned in Chapter 4, in situ annealing has also been suggested to improve the efficiency of bulk dilute nitride solar cells [115]. This creates complications while growth of multi-junction systems as growth of cells above 1eV cell would necessarily involve higher growth temperatures.

Recently, promising results have been obtained (see Fig.5.1) by the growth of bulk GaInAsN as the i-region in a GaAs solar cell [116], as well as bulk junction [117].
5.3 Analysis of Dilute Nitride MQW solar cells

From the literature, based on the presence of trap states, sensitivity to annealing, and the dependence of photocurrent on depletion region indicates that it is advisable to use nano-structured dilute nitrides within the i-region of GaAs to serve as a solar sub-cell for multi-junction applications. Attempts to fabricate strain-balanced [118] as well as lattice matched [119] InGaAsN multi-quantum well solar cells have identified the incomplete carrier escape as a major impediment to solar cell performance.

The absorption coefficient obtained for a multi-quantum well in experimental data [8] as a function of bias can be seen in Fig. 5.2. There is significant improvement of spectral response with increasing negative bias, saturating at -0.9 V. As the electric field is increased in the i-region, carriers are swept out of the depletion region and harnessed.
Figure 5.2: Dependence of spectral response of a GaAs$_{0.981}$N$_{0.019}$/GaAs MQW solar cell on applied voltage, showing an increased carrier collection upon reverse bias [8].

It is clear that a way to obtain higher current is to improve carrier collection. One way to achieve this without sacrificing the open circuit voltage is through a process called resonant tunneling.

5.4 Effect of Thermally assisted Resonant Tunneling

First investigated in the 1970’s [120] [121], resonant tunneling has been known in semiconductor double-barrier (or QW) systems to be caused by tunneling of charge carriers through a sequence of potential wells. A modification of resonant tunneling,
which is of interest to us, is sequential resonant tunneling, where the \( n \)\textsuperscript{th} energy level in one QW lines up with the \( n+1 \)\textsuperscript{th} energy level of the next QW (See Fig. 5.3).

![Sequential Resonant Tunneling Through QW's](image)

Figure 5.3 Traditional sequential resonant tunneling through QW’s, with (a) \( n \)\textsuperscript{th} level being resonant with the \( n+1 \)\textsuperscript{th} level and (b) \( n \)\textsuperscript{th} level being resonant with the \( n+2 \)\textsuperscript{th} level, from [122].

It can be seen from the literature that sequential resonant tunneling with majority carriers was used to create infrared laser amplifiers [123], quantum cascade lasers [124], and also quantum well solar cells [125]. Hence there is an increase in the current generation through the MQW or superlattice system. For the GaAsN/GaAs MQW solar cell, it is important to obtain the carriers as close to the conduction band as possible to preserve a good \( V_{OC} \), hence a resonant tunneling design can be used in the opposite sense, i.e. along the electric field, the \( n+1 \)\textsuperscript{th} energy level of one QW is resonant with the \( n \)\textsuperscript{th} energy level of the next [126] (See Fig. 5.4). In this design, thermal up-conversion of minority carriers transition within the QW is facilitated by thermal energy within the solar cell, hence the process is also known as \textit{thermo-tunneling}. 

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As it can be seen, since the valence band-offset for holes in GaAsN (~0.01 eV) is much smaller than that of the electrons (~0.4 eV), energy level alignment is important only for electrons. The value for thermal escape lifetime and tunneling lifetime of carriers are given by:

\[
\frac{1}{\tau_{\text{thermal}}} = \frac{1}{L_w} \sqrt{\frac{k_B T}{2\pi m_w}} \exp \left( - \frac{E_{\text{barr}}(F)}{k_B T} \right) \tag{5.1}
\]

\[
\frac{1}{\tau_{\text{tunneling}}} = \frac{n \hbar}{L_w^2 2m_w} \exp \left( -\frac{2}{\hbar} \int_0^b \sqrt{2m_b(qV(z) - E_n - qFz)}dz \right) \tag{5.2}
\]

Where \(E_{\text{barr}}(F)\) is the energy of the barrier (GaAs) as a function of the electric field strength \(F\), \(m_w\) and \(m_b\) are effective mass of electrons in the well and barrier respectively.
The net carrier escape lifetime is given by:

\[
\frac{1}{\tau_{total}} = \frac{1}{\tau_{esc}} + \frac{1}{\tau_{recombination}} = \frac{1}{\tau_{thermal}} + \frac{1}{\tau_{tunnel}} + \frac{1}{\tau_{recombination}} \quad 5.3
\]

Carrier escape requires:

\[\tau_{esc} < \tau_{recombination} \quad 5.4\]

For this work, recombination lifetimes were extracted from the dependence of spectral response of IQE on carrier lifetimes as [127]:

\[
IQE = \frac{1}{\frac{1}{\tau_{esc}} + \frac{1}{\tau_{recombination}}} = \frac{\tau_{total}}{\tau_{esc}} \quad 5.5
\]

Since the dependence of IQE on the number of QW’s can be extrapolated from previous data, it was only necessary to calculate the escape time, and utilize the equation to obtain \(\tau_{recombination}\). In order to estimate carrier escape times, energy levels were first calculated as a function well width and nitrogen concentration. From the calculations for obtaining a 1eV solar cell, carrier escape times can be obtained as a function of the relevant material width i.e. barrier width for tunneling, well width for thermal escape. As shown in Fig 5.5, this provides a range of well width suitable for tunneling. Further, the design of a resonant tunneling system was seen to reduce carrier escape time due to the short tunneling lifetimes.
It can be observed that for barrier widths < 5 nm, the carrier escape is mainly tunneling-escape-dominated, while that for > 5 nm is thermal-escape-dominated, which prevents extraction from progressively deeper levels (Fig. 5.6).

Figure 5.6 Carrier thermal escape lifetime is obtained as a function of energy level position, and is compared with the calculation of energy levels for a 1eV GaAsN QW. For escape from a deep level (1.05 eV) it takes 5 ns, which is >τ_{recomb}.
5.5 Simulation of resonant thermo-tunneling MQW solar cell

Several different choices are available for designing a resonant tunneling system. One can vary the well thickness, or the nitrogen content, in order to vary the energy level positions. Due to ease of growth, a constant nitrogen concentration with varying well width is generally preferred. An example of a 3QW resonant tunneling system is shown in Fig. 5.7, along with its energy level diagram in Fig. 5.8, indicating the thermionic and tunneling escape times of the system.

Figure 5.7 Design of resonant tunneling sequence of well widths for GaAs$_{0.971}$N$_{0.029}$ QW/5nm barrier GaAs ($F=35$ kV/cm), showing thermal transitions (vertical bold arrows) and tunneling transitions (horizontal dashed arrows) and calculated QW widths to obtain resonance.
Figure 5.8 Thermal-assisted resonant tunneling process for the design showed in Fig. 5.7. Thermal escape lifetimes reduce for transitions of smaller energy gaps. Vertical (bold) arrows and horizontal (dashed) arrows show thermal and tunneling transitions respectively. The block-arrow indicates an order-of-magnitude shift in escape times compared to Fig. 5.6.

Utilizing the resonant thermo-tunneling design, the spectral response or IQE can be calculated, and utilized to estimate the efficiency improvement in a multiple-junction solar cell. This is done by calculating the spectral response using the drift diffusion model (Appendix A) and the methodology outlined in Section 3.4.2.

5.5.1 Spectral Response and IV characteristics

Under ideal conditions, (carrier extraction efficiency factor n=1) with increase in number QWs, the spectral response must increase. Fig. 5.9 gives the dependence of spectral response of this system as a function of QW periods, for a GaAs$_{0.971}$N$_{0.029}$/GaAs(1eV) MQW solar cell for full carrier escape (IQE=1). As expected, the spectral response increases with the number of QWs, enabling the absorption of greater flux of photons.
Figure 5.9 Calculation of Spectral Response (EQE) of 1eV GaAsN(2.9%)/GaAs MQW Resonant Tunneling device as a function of QW periods. Data between wells has been interpolated for clarity, and positions of e-hh1,e-lh1,e-hh2,e-lh2 indicate transitions between heavy holes, light holes and electronic energy levels. At 300K $E_g$(GaAs) = 1.42 eV

In order to extend the calculation for a non-ideal multi-quantum well system, we require the realistic value for both $\tau_{recombination}$ and $\tau_{escape}$. For a system with $N$ QWs, we can obtain the net Spectral Response or IQE efficiency factor $n$ as:

$$n = IQE(N) = IQE(1)^N = \left(\frac{\tau_{total}}{\tau_{esc}}\right)^N$$

Hence, for a 15-period QW system with $IQE(N) = 0.41$, we can obtain $\frac{\tau_{total}}{\tau_{esc}}$ to be 0.942. Using carrier escape times calculated for thermionic escape from Fig.XX, $\tau_{recombination}$ can be found to be ~0.5 ns. This value can now be used for calculation of IQE for any general resonant tunneling system, according to the following outline:

1. Calculate absorption coefficient for a single QW
2. Obtain escape sequence, using $N_{RT}$ coupled-wells, from energy level diagram
3. Calculate total carrier escape time for $N_{RT}$ coupled wells

4. Calculate total escape time by including recombination

5. From the ratio, calculate the ideality factor for $N$ sets of $N_{RT}$ coupled wells.

Accordingly, the absorption for a 3QW coupled system ($N_{RT} = 3$) could be calculated. The effect of the electric field is vital for calculation of escape time, as a slight offset of the resonant energies drastically reduces the coupling between the wells, and hence the absorption. As an example, the dependence on the carrier extraction efficiency on the thickness of the barriers of a 3QW system with 2.2nm, 7nm and 14 nm QWs is given in Fig. 5.10.

![Figure 5.10: Carrier escape probability as a function of barrier thickness for a 3QW resonant tunneling design.](image)
5.5.2 Simulation of Efficiency of Tandem Solar Cells

Method for calculation of efficiency of a multi-junction system has been shown in section 2.3.3. Estimated IV characteristics for a 4 junction cell InGaP/GaAs/GaAsN(MQW)/Ge with a 24 period QW is given in Fig. 5.11, both with and without improvement via resonant tunneling coupled well design involving 3QW.

Figure 5.11: Simulated I-V characteristics of a 4J GaInP/GaAs/GaAsN(MQWSC)/Ge solar cell. Dashed line shows the response of 24 6nm QW/15 nm barrier system, assuming full escape, while dash-dotted line utilizes calculated escape time. The improved resonant tunneling design (bold) has 24 QW (8 triple-QW systems with 4nm barrier)

Using a realistic Drift-diffusion model, as described in Appendix A, the I-V characteristics and hence the efficiency of a 4-junction solar cell with 3rd sub-cell being a 1eV dilute nitride MQWSC is obtained both with and without thermally-assisted resonant tunneling design. A slight improvement in the current extraction as compared to traditional MQW system is expected from the simulation.
Efficiency of a MQW system depends critically on the number of QWs due to current matching considerations. The two competing phenomena are the strength of the electric field in the intrinsic region and the strength of the absorption of the QWs. A calculation of the dependence of efficiency under both standard conditions and concentration is given in Fig. 5.12.

![Figure 5.12: Efficiency as a function of number of coupled QWs for 4J GaInP/GaAs/GaAsN(MQW)/Ge system under 1 sun AM0 and 500 sun concentration.](image)

It can be seen that efficiencies of up to 39% under 1 sun and 49% under concentration are possible with this structure, vastly improving current state of the art for multi-junction systems.

### 5.6 Growth and Characterization of Resonant Tunneling MQW Solar cells

To further test the design, a series of samples were grown with both conventional and
resonant tunneling design. The concentration of nitrogen was optimized to obtain 1eV band-gap (~3%), and the run-vent system described in Chapter 4 was used throughout the growth. Processing of the samples was done by photolithography of gold front contact and thermal evaporation of a uniform back contact on the samples. A short summary of the samples to be discussed here is given in Table 2. A schematic of Sample 1 is given in Fig. 5.13.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Resonant Tunneling Design</th>
<th>No. of QW’s</th>
<th>Coupled QW sets</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBE 1 (3.2%)</td>
<td>Yes</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>MBE 2 (3.1%)</td>
<td>Yes</td>
<td>12</td>
<td>3</td>
</tr>
<tr>
<td>MBE 3 (2.8%)</td>
<td>Yes</td>
<td>24</td>
<td>3</td>
</tr>
<tr>
<td>MBE 4 (2.9%)</td>
<td>No</td>
<td>24</td>
<td>None</td>
</tr>
</tbody>
</table>

5.6.1 Sample 1

Figure 5.13: Schematic of sample 1, a p-i-n GaAs structure with 4 sets of 2QW’s inserted into the 288 nm thick intrinsic layer, along with its corresponding carrier dynamics. Expected carrier escape time (tunneling+thermal escape) ~5 ps.
The quality of this growth was analyzed using transmission electron microscopy (TEM) techniques. High-resolution phase-contrast TEM images were taken using a JEM-4000 EX high-resolution transmission electron microscope operated at 400 keV, with a structural resolution of 1.7 Å (see Fig. 5.14).

![Figure 5.14: A cross sectional TEM image (taken using JEM-4000) of sample 1 showing the presence of 8 QW as per design. The white layer on top of the QW’s marks the AlGaAs window layer. TEM courtesy D. Tang (ASU).](image)

Accuracy of the growth structure was also confirmed by studying the detail of QW thickness, as shown in Fig. 5.15. It was seen that the growth thickness obtained (4.1 nm
and 5.8 nm) was close to the required values. Phase contrast in the images indicated the presence of nitrogen as interstitials.

Figure 5.15 Close-up of the 4\textsuperscript{th} QW set (from the top) indicating the position of the 6nm (top) and 4nm (bottom) QW respectively.

Photoluminescence analysis of the sample gave a high intensity for GaAsN, almost comparable to that of GaAs, showing the good quality of the interface structure (Fig. 5.16). Sample 1, which was grown with the modified run-vent system, shows a distinct improvement in the GaAsN response comparable to bulk GaAs layer in the linear scale even prior to any thermal processing. Energy of the QW’s is observed to start at about 1.1eV. There is a shoulder to the right of the GaAs peak due to e-neutral carbon acceptor. The peaks at 1.28 eV (QW1) and 1.31 eV (QW2) correspond to the positions of the fundamental energy levels of 6nm and 4 nm QWs respectively, while the peak 1.34 eV (QW3) corresponds to the 1\textsuperscript{st} excited level of 6nm QW. There is no signature of interface
contamination at 1.34-1.40 eV in this sample, in contrast to its twin grown with conventional plasma setup. This shows that the run-vent system has most likely prevented the formation of a parasitic layer at the GaAsN/GaAs interface.

Figure 5.16 10K Photoluminescence of GaAs$_{0.979}$N$_{0.021}$ QW samples using (a) conventional shutter activated operation, with growth interruption prior to start of GaAsN growth (Sample B), by (b) gate valve operated run-vent system without growth interruptions. (Sample 1)

In order to obtain the carrier extraction obtained by resonant tunneling setup, spectral response was done with sample 1 (Fig. 5.17). In contrast to previous results where the spectral response depended quite critically on external bias, it is seen that there is very little effect of voltage on spectral response of sample 1 (<0.05%) indicating full carrier extraction from the quantum wells. While for 990 nm the spectral response (External Quantum Efficiency, or EQE) increased with bias, for 970 nm it decreased, showing that the solar cell carrier extraction is close to the maximum, with a shift in the peak caused due to electric field of the applied voltage. A comparison of the two results is shown in Fig. 5.18.
Figure 5.17: External Quantum Efficiency (EQE, a fraction of 1) of sample 1, a 1eV GaAsN resonant tunneling (RT) MQW solar cell as a function of external bias varied between -0.4 V to 0.4 V. There is no difference in absorption above the band-gap (below 871 nm) however there is a slight (<0.5%) variation in absorption from dilute nitride material, shown for ~970 nm in the lower graph.
Figure 5.18 A decrease in EQE with bias at 970nm, compared with an increase at 990nm. In both cases, $\Delta$EQE~0.05% (*courtesy, A Maros, ASU*).

The decisive characterization of a solar cell is obtained by its I-V curve. For a 0.023 cm$^2$ cell under 1 sun AM0 conditions, the IV curve obtained is shown in Fig. 5.19. It is seen that a very high $V_{OC}$ is obtained (625 mV). The values varied between 480 mV to a maximum of 636 mV.

Figure 5.19: Current voltage characteristics of 8 period 2QW resonant tunneling structure (Sample 1) with high $V_{OC}$. 

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Figure 5.20: Statistics of IV data from Sample 1 showing the spread of values obtained for $V_{OC}$.

Thus, it was possible to obtain good quality MQW solar cells, the statistical distribution of whose data is given in Fig. 5.20.

5.6.2 Sample 2

This design was further confirmed by the growth of a similar structure, with coupled 3QW (and hence a total of 12) instead of two, as shown in the schematic in Fig. 5.21.

Figure 5.21: Schematic of sample 2, showing the design of 3QW resonant tunneling structure with expected escape times.
Photoluminescence analysis of this structure revealed characteristics similar to the previous sample, but with greater FWHM of the peaks possibly due to increased defect density (Fig. 5.22). Luminescence intensity of GaAsN region is still comparable to the GaAs region, while the transitions to higher energy levels of QW’s picking up at lower temperature, showing a greater probability of escape at room temperature (300K).

Figure 5.22: Photoluminescence (PL) intensity as a function of temperature for Sample 2, showing the standard Varshni shift of the main absorption peak (1.42 eV at 300K), and QW transitions at 1.17 eV and 1.35 eV at 10 K.

A comparison of the IV characteristics of the two samples is shown in Fig. 5.23, which are identical in all respects except for intrinsic region thickness due to change in the number of QWs. It can be seen that the voltage remains unchanged, while the current extraction improves with the addition of a QW to the resonant tunneling system. Similarly, for samples 3 (Resonant tunneling 8 sets of 3QW) and 4 (24 QW with 5 nm barrier), the comparison of IV characteristics (Fig. 5.24) shows a slight increase in
current extraction for the resonant-tunneling system. The sharp increase in open circuit voltage is yet to be verified.

Figure 5.23: IV-characteristics of sample 2 (red triangle) as compared to sample 1 (black square) showing a relative increase in current extraction.

Figure 5.24 IV-characteristics of sample 4 showing a relative increase in current extraction of the resonant tunneling device.
5.6.3  **Comparison with Device Simulation**

In order to further verify the characteristics obtained for the device sample 1 with a high open circuit voltage, using the drift-diffusion method the efficiency was estimated under the following assumptions (a) the top layer of GaAs (520 nm) is retained above the solar cell (See Fig. 5.14) and (b) the open circuit voltage is fit to what is called the radiative limit (for complete carrier extraction) which lies ~0.4 eV below the band-gap.

![Graph showing simulated and experimental current voltage characteristics of a 4 period 2QW solar cell under 1 sun AM0. The radiative limit for a ~1.1 eV cell is indicated at 700 meV.](image)

When compared with previous measured open-circuit voltages of Ga(In)AsN system it is observed that the $V_{oc}$ obtained approaches the radiative limit much closer for this sample.
This is also consistent with previous observations for quantum well solar cells in general [46].

An improved Voc coupled with improved carrier extraction would make the resonant tunneling system ideal for a 1eV sub-cell in a 4-junction system, enabling the projected high efficiency of ~40% under 1 sun concentration.

5.7 Summary

Following experimental data, it was observed that dilute nitride MQW solar cells suffered
from incomplete carrier extraction. In order to overcome this barrier, sequential thermally-assisted resonant tunneling design was proposed. Calculations were done using drift-diffusion method to determine realistic efficiency of multi-junction solar cells with this design, and the results showed a promising 39% (1 sun AM0) and 49% (500 sun AM0) respectively.

Growth of samples with and without resonant tunneling structures was undertaken with the improved nitrogen plasma setup discussed in Chapter 4, which gave high-luminescence dilute nitride solar cells. TEM characterization helped determine the accuracy and interface sharpness of MQW growth, while IV characterization indicated high \( V_{OC} \) solar cells. Study of bias-dependent spectral response helped ensure that carrier extraction is saturated, while comparison of IV characteristics helped determine the effect of increase in QW period as well as design of coupled QWs. Finally, a fit of the experiment to theoretically calculated current-voltage characteristics showed that the resonant tunneling system shows high carrier escape and hence, open circuit voltage that approached closer to the radiative limit.
In photovoltaics, highest efficiencies obtained recently have focused on absorbing a greater range of incident solar energy by the use of III-V multi-junction solar cells. In this field, there is a pressing need for a cell of band-gap 1eV in order to enhance efficiency. Among other solutions for this problem, the unconventional band-gap behavior of III-V dilute nitrides has offered a feasible path to achieve this. Since lattice-matched systems are preferred for multi-junction applications, attempts have been made to create lattice matched 1eV Ga(In)AsN solar cells to work as a 3rd of 4th junction.

However, the degradation of minority carrier lifetimes, reduction in diffusion length and doping issues have restricted their widespread development. One way to overcome this problem has been to insert dilute nitride quantum wells smaller than the diffusion length within the intrinsic region of a p-i-n GaAs solar cell, enabling absorption below the GaAs band-gap. Prior state-of-the-art in this regard had involved fabrication of dilute nitride MQW solar cells, where it was observed that incomplete carrier extraction from the QW region restricted current response of the cell.

In order to design suitable quantum well systems to improve upon those results, in this work, band structure of dilute nitrides was calculated taking into account contributions from effect of strain and pressure on the band-gap. Thereafter, energy levels in the quantum well region were calculated followed by determination of absorption properties of a single quantum well in an MQW system, taking into account contributions from bulk
GaAs, the quantum well region and excitonic absorption. Calculation of the absorption coefficient was used to simulate the expected quantum efficiency (spectral response) of a MQW system. Comparing this with experiment provided an estimate of the carrier extraction, showing that the assumption of 100% carrier escape, considerably overestimates the actual value of IQE.

In order to investigate properties of previously grown GaAsN samples, HRXRD, PL and TEM characterization was done on them. XRD gave information about composition and strain in the system, while PL results showed the presence of a lower composition nitridation layer, possibly at the interface of GaAsN/GaAs. High resolution TEM confirmed the presence of nitrogen at the interface. Since growth of dilute nitrides by epitaxy involves the use of nitrogen plasma source, it was hypothesized that nitridation was occurring when the plasma source was fired up, especially during growth interruptions. Since conventional plasma operation fails to prevent a leak of nitrogen into the chamber even with the valve closed, an improved design using gate-valve-activated run-vent system of pumping was installed to achieve better nitrogen flux transitions. This improved the quality of growth, enabling sharper transitions of nitrogen flux, and growth of multi-quantum-well samples whose luminescence from the dilute nitrides matched that of single crystal GaAs.

Following these experimental and theoretical results, a way of improving carrier extraction by using thermally assisted resonant tunneling was investigated. Initial theoretical projections showed that it was possible to obtain efficiencies of 39% (1 sun
AM0) and 49% (500 sun AM0) using this design, and small improvement in carrier extraction was expected. In order to test these estimates, a series of resonant tunneling MQW solar cells were fabricated. The results showed a clear improvement of carrier extraction, as verified by bias dependent spectral response. One design for MQW gave a higher open-circuit voltage for the 1eV cell compared to previous works in the literature.

6.1 Outlook

Future work in this topic would involve determining the detailed carrier dynamics of the solar cell. This would involve the extraction of carrier mobility, and carrier lifetime determination by either time-resolved PL or bias dependent spectral response, in order to correlate data from both sources. Systematic optimization of the electric field within the intrinsic region by varying the intrinsic region thickness for a specific design of resonant tunneling structures will give a clear dependence of carrier extraction and open circuit voltage on the electric field, parameters that are vital for solar cell performance. Upon the design of a suitable single junction solar cell, further research can be done in order to determine the efficiency of the cell in a multi-junction setup, in order to target ~40% efficient photoconversion.
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Appendix A: Drift Diffusion Model of a Solar Cell

A.1. Drift Diffusion Equations

The semi-classical transport of charges can be explained using BTE (Boltzmann Transport equation). However, the direct analytical solution of the BTE is difficult for device simulation. Therefore the predominant model called Drift Diffusion model is generally used for traditional semiconductor device modeling. In this model the electric fields and spatial gradient of the carrier density is localized i.e. the current at a particular point only depends on the instantaneous electric field and concentration gradient of carriers at that point.

The drift diffusion equations can be obtained by solving the BTE (Boltzmann Transport equation) by solving for the moments of this equation. For steady-state and 1D geometry, the use of relaxation time approximation for the BTE results in the following equations for electron and hole current densities:

\[ J_n(r) = \mu_n n \nabla E_{F_n} \]
\[ J_p(r) = \mu_p p \nabla E_{F_p} \]

A.1

Where \( \mu_i \) is the mobility of species \( i \), \( n \) and \( p \) are the carrier concentrations, and \( E_{F_n} \) is the energy of the quasi-fermi level. In a compositionally invariant material, we have to take into account only the presence of the electrostatic field, reducing the equation A.1 to:
Where $D_n$ and $D_p$ are given by the Einstein relations relating mobility to the diffusion constant under low field conditions:

\[
\mu_n = \frac{qD_n}{k_B T}, \quad \mu_p = \frac{qD_p}{k_B T}
\]

With conditions of continuity, the change in carrier concentrations is given by:

\[
\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} + G_n - U_n \quad \text{A.4}
\]

\[
\frac{\partial p}{\partial t} = -\frac{1}{q} \frac{\partial J_p}{\partial x} + G_p - U_p
\]

Where $G_i$ refers to the generation and $U_i$ the losses, or recombination of carriers. At steady state, the time derivatives go to zero, giving:

\[
D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx} + \mu_n n \frac{dF}{dx} + G_n - U_n = 0 \quad \text{A.5}
\]

\[
D_p \frac{d^2 p}{dx^2} + \mu_p F \frac{dp}{dx} + \mu_p p \frac{dF}{dx} + G_p - U_p = 0
\]

Where $F$ is the electric field. Once more, using the Einstein relations, one obtains:

\[
\frac{d^2 n}{dx^2} + \frac{qF}{k_B T} \frac{dn}{dx} + \frac{G(x)}{D_n} \frac{n-n_0}{L_n^2} = 0 \quad \text{A.6}
\]

\[
\frac{d^2 p}{dx^2} + \frac{qF}{k_B T} \frac{dp}{dx} + \frac{G(x)}{D_p} \frac{p-p_0}{L_p^2} = 0
\]
The carrier diffusion lengths are given by:

\[ L_n = \sqrt{\tau_n D_n} \quad \text{A.7} \]
\[ L_p = \sqrt{\tau_p D_p} \]

Where \( \tau_p \) and \( \tau_n \) are the carrier lifetimes in the material. If the carrier concentration is uniform for a specific region, for depletion widths \( w_p \) and \( w_n \), we can obtain the general solutions of Eq. A.6 as:

\[ n(E,x) = A_n \cosh\left(\frac{-x - w_p}{L_n}\right) + B_n \sinh\left(\frac{-x - w_p}{L_n}\right) + Y_n e^{-\alpha(x - x_p)} \quad \text{A.8} \]

Where:

\[ Y_n = \frac{\alpha(1 - R)b_s L_n^2}{D_n(\alpha^2 L_n^2 - 1)} \quad \text{A.9} \]

The boundary conditions for the depletion region are given by:

\[ n - n_0 = \frac{n_i^2}{N_a} \left(\exp\left(\frac{qV}{k_BT}\right) - 1\right) \]
\[ D_n \frac{dn}{dx} = S_n (n - n_0) \quad \text{A.10} \]

Where \( S_n \) is the surface recombination velocity. The electron current generated is given by:
A similarity expression is derived for the p-type region. For current in the space charge region, one can derive:

\[
J_n(E, -w_p) = \frac{\alpha q (1 - R) B_0 L_n}{a^2 L_n^2} e^{-\alpha(x_p - w_p)} \left( \text{cosh} \left( \frac{-x_p - w_p}{L_n} \right) \frac{S_n L_n}{D_n} + \text{sinh} \left( \frac{-x_p - w_p}{L_n} \right) - \frac{S_n L_n}{D_n} - \alpha L_n \right) + a L_n \right) \right) \times \left( \text{cosh} \left( \frac{-x_p - w_p}{L_n} \right) \frac{S_n L_n}{D_n} + \text{sinh} \left( \frac{-x_p - w_p}{L_n} \right) \right)
\]

\[
+ \frac{q D_n n_0}{L_n} \left( e^{q V/kT} - 1 \right) \left( \text{cosh} \left( \frac{-x_p - w_p}{L_n} \right) \frac{S_n L_n}{D_n} + \text{sinh} \left( \frac{-x_p - w_p}{L_n} \right) \right)
\]

Thus the overall I-V characteristics of a realistic solar cell can be calculated for emitter and base thickness of \(w_p\) and \(w_n\) respectively.

\[
J_{scr}(V) = q n_i \left( \frac{w_n + w_p}{\sqrt{\tau_n \tau_p}} \right) \frac{2 \sinh \left( \frac{q V}{2 kT} \right)}{q (V_t - V)/kT} \pi
\]

\[
- q \int (1 - R) B_0 e^{-\alpha(x_p - w_p)} \left( 1 - e^{-\alpha(w_n + w_p)} \right) dE
\]

Thus the total current for a p-i-n junction is given by:

\[
J(V) = J_{scr}(V) + \int j_n(E, -w_p) dE + \int j_p(E, -w_n) dE
\]
Appendix B Optical Characterization

B1.1 Photoluminescence Spectroscopy

Photoluminescence is a non-destructive method of probing the electronic properties of materials such as band gap, impurity, and defect levels, etc. When a light source of sufficient energy, such as a laser, is incident onto the material, carriers from the valence band are excited to higher levels than the conduction band and photoluminescence (PL) is emitted when these photo-excited carriers return to their equilibrium states. The energy of the emitted light depends on the relative difference of energy between two electron states involved in the transition between the excited state and the equilibrium state. These states can be excitonic states, impurity levels, defect levels, conduction, or valence band states, etc. Photoluminescence is used to characterize various material properties:

1. Band-gap: Generally, the radiative transition in direct-band gap materials occurs between valence band ground states and excited conduction bands at k=0. The energy difference gives the band-gap of the material.

2. Impurity and Defects: Radiative transitions below the band-gap can also be identified, due to localized defect or trap states between valence and conduction bands. By determining their dependence on temperature and the Arrhenius plot for the variation, activation energy of various defect states can be identified.
3. Recombination mechanisms: Determination of the carrier dependence of luminescence intensity helps establish the radiative or non-radiative nature of the recombination mechanisms, including differentiation between Shockley-Read-Hall and Auger processes.

The PL system we used in our studies is shown in Figure B.1. A Milles-Griot red Laser of wavelength 632.8 nm Laser was used. The sample is placed in a helium-cooled Janis cryostat, which can go as low as 10 K. A heater and a temperature controller unit are used for the temperature control of the samples during PL vs. temperature studies. The laser light is fine tuned with highly precise optics before entering the cryostat entrance. The PL signal from the sample is focused using two lenses at the entrance of a Triax 320™ monochromator and was detected by either InGaAs or Si detector after the monochromator. The collected spectral signal was locked to the given frequency using a chopper and Stanford lock-in device to avoid undesired white noise from the stray light and ac power frequency while a computer that controls the configuration of the monochromator, records the data.
Figure B.1: Lab setup for Photoluminescence characterization
B1.2 Spectral Response

The Spectral Response is measurement of photovoltaic devices is an important characteristic currently performed in the design and fabrication process of each of these devices. Also called the External Quantum Efficiency (EQE) of a solar cell, it is vital in characterizing the absorption properties of the system.

The spectral response at a given wavelength $\lambda$ is $J(\lambda)/I(\lambda)$ where $J(\lambda)$ is the total photogenerated short circuit current density at a given wavelength, and $I(\lambda)$ is the spectral irradiance of the given light. The photogenerated current is measured at several wavelengths using monochromatic light from a filtered light source.

The spectral response of a test cell can be measured by the direct comparison of the output of the test cell, with a calibrated spectral response of the reference cell, when a changing component of monochromatic light hits the test cell and the reference cell alternatively. A monochromator and a filter wheel are used as the monochromatic light source, and the exit beam is chopped at a given frequency. The test and reference cells are mounted suitably and arranged to be illuminated and measured for a given wavelength of the incident beam. The output is then measured through the system of lock-in amplifier, which is locked to the chopper frequency. Additional Spectral Response measurements were conducted with Standard ORIEL IQE 200™ setup (Fig. B.2) available from Dr. Pavel Datta at Energy Research Park, University of Houston.
Figure B.2: Oriel IQE 200 setup used for EQE measurements
B1.3 I-V Measurements

Dark I-V and illuminated I-V measurements are crucial characterization methods for determining the quality of the solar cell. I-V measurement provides information about efficiency of the solar cell, open circuit voltage, short circuit current, series and shunt resistance estimates, as well as the response to concentration.

An Oriel™ Solar Simulator was used in our lab in conjunction with a Keithley 2400 source meter that generates the voltage for the full range of measurement. An integrated LabVIEW software was utilized to extract the information from the source meter. The Solar Simulator could be used to generate both AM0, and AM1.5 spectra.

Figure B.3: Oriel Solar Simulator with 4-probe setup for I-V measurements.
Appendix C: Post-Growth Processing of the Device

C.1. Chemical Processing of the Device

To prepare the newly grown wafer into a device, various processes of chemical processing have to be performed: cleaning of the samples, close contact photolithography, metal contact vapor deposition by thermal evaporation and thermal wet etching. All processes were performed in Class 100 Clean Room Facility of Center for Advanced Materials, University of Houston.

The device was first cleaned, immersing in baths of boiling trichloroethylene, cold acetone and boiling methanol sequentially. A thin coat of Futurex-NR7-3000 PY chemical photo-resist was applied to the front surface of the device. A Laurrell Technologies Corporation (WS-400B-GNPP/LITE) spinner was used (Fig C.1), with rotations at 3000 rpm and 5000 rpm for 25 s each.

Once the resist was set by heating on a hot plate, the sample was exposed to UV light for 90 s, through the appropriate Mask Plate, using a Karl Suss (MJB3) mask aligner, as shown in Fig. C.2. The device was then developed for 20 seconds, using a Futurex Developer (RD6), after baking it for another minute at 110 C.
Figure C.1: Laurrell Technologies Corporation Spinner (WS-400B-GNPP/LITE)

Figure C.2: Karl Suss (MJB3) UV Mask Aligner
The device was then placed on a thermal evaporator (Key Hass) to deposit gold contact of ~1000 Å on the front and ~2000 Å on the back. A lift-off procedure was then performed to remove the non-patterned gold, by washing with acetone, swirling the sample in an acetone bath, and hard spraying the acetone onto the sample.

Figure C.3: Thermal Evaporator.

For the isolation of the cells, lithography was done using a positive photo-resist (Shipply 1818). A thin layer of the photo resist material was spread on the device, using a spinner rotation of 3000 rpm for 20 seconds, 5000 rpm for 25 seconds, followed by baking for 1 minute at 110 °C. The device was then exposed to UV for 90 seconds, and developed using a Shippley Developer 321 for 3 minutes, before the hard bake at 110 °C. A solution
with 5:1:1 ratio of sulfuric acid, hydrogen peroxide and DI water was used for the mesa etching, which etches GaAs at the rate of 0.1 micron/minute. Finally the contact layer is removed using a 4:1 Ratio solution of citric acid and hydrogen peroxide.

C.2. Rapid Thermal Processing

Rapid thermal processing, also referred to in the manuscript as rapid thermal annealing (RTA) is a process where the sample is heated very quickly (< 60 seconds) to temperatures of ~ 800 C, followed by cooling. RTA was done using an RTP-600 S system by Model Process Technology Corporation (Rev. 2.0) under nitrogen and argon flow. The sample was placed between two high-resistivity plates, generally sandwiched between Si or GaAs depending on the sample, and various recipes were used to for the 2 stage ramp of the temperature, from 0-350 C, and then from 350-800C respectively.

Figure C.4: Rapid Thermal Processing (RTP-600S) setup
Figure C.4: Example of RTA recipe.