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Growth and Characterization of Type-II Submonolayer ZnCdTe/ZnCdSe Quantum Dot Superlattices for Efficient Intermediate Band Solar Cells

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Growth and Characterization of Type-II Submonolayer ZnCdTe/ZnCdSe Quantum Dot Superlattices for Efficient Intermediate Band Solar Cells

by

Siddharth Dhomkar

A dissertation submitted to the Graduate Faculty in Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

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This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation proposal requirements for the degree of Doctor of Philosophy.

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THE CITY UNIVERSITY OF NEW YORK
Abstract

Growth and Characterization of Type-II Submonolayer ZnCdTe/ZnCdSe Quantum Dot Superlattices for Efficient Intermediate Band Solar Cells

by

Siddharth Dhomkar

Adviser: Professor Igor L. Kuskovsky

In this thesis, we discuss the growth procedure and the characterization results obtained for epitaxially grown submonolayer type-II quantum dot superlattices made of II-VI semiconductors. The goal behind this study is to show the feasibility of this novel material system in fabricating an efficient intermediate band solar cell.

Intermediate band solar cells can potentially have an efficiency of 63.2% under full solar concentration, but the material systems investigated until now are far from optimum and are fraught with growth related issues including low quantum dot densities, presence of wetting layers, strain driven dislocations etc. Here, we have investigated a novel material system grown via migration enhanced epitaxy with stacked type-II ZnCdTe submonolayer quantum dots embedded in ZnCdSe matrix and having close to the optimal material parameters required for an IB material. Upon optimizing growth conditions for ZnTe/ZnSe multilayer quantum dot systems, the growth parameters were modified so as to obtain various ZnCdTe/ZnCdSe samples grown on InP substrates. An extensive characterization has been performed to investigate structural, optical as well as electrical properties of these multilayered structures. Finally, a preliminary device fabrication has been performed, which will provide definite guidelines towards optimization of an actual intermediate band solar cell structure.

To restate, the objective of this thesis is to demonstrate successful growth and characterization of multilayer structures with embedded submonolayer type-II quantum dots in order to explore the possibility of employing them as an intermediate band material, with the goal of engineering an ultra-efficient intermediate band solar cell.
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Chapter 1

Introduction

1.1 Significance of the Study

Utilization of solar energy is one of the promising and sustainable ways to produce electricity. In conventional solar cells (SCs), solar photons having energy same or more than the band gap energy of the semiconductor, excite electrons from the valence band (VB) to the conduction band (CB). Once the electrons (or holes) are in the CB (or VB), they flow outside the semiconductor through a selective contact forming an electric current at a specific potential outside the cell. The charge carriers then lose their energy by acting as a power source and the lower energy electrons (or holes), are consequently fed back to the semiconductor VB (or CB) through another selective contact [1].

There is a fundamental trade-off between current and voltage output of a single junction SC arising from the losses due to forbidden below band gap absorption and the thermalization of hot carriers [2–4]. This enforces a limits over the ultimate efficiency of an ideal single junction SC, making photovoltaic conversion relatively expensive (detailed description is given in the following section). Thus novel concepts are required either to reduce the fabrication costs (CdTe [5], CIGS [6], pervoskite [7]) or to increase the efficiency [8, 9] (multi-junction [10], multiple carrier generation [11], hot carrier [12] and intermediate band (IB) [13]).

In this thesis, the concept of IB-SCs based on type-II submonolayer quantum dots
(QDs) has been explored. It has been demonstrated that the investigated material system is potentially an ideal material system for ultra-efficient SCs.

The first chapter briefly reviews the fundamental concepts and the scientific terminologies required for the later discussions, whereas the second chapter consists of a brief overview of all the experimental techniques used for the characterization. The third chapter describes the process of investigation leading to the important results. Finally, the last chapter summarizes the key findings as well as examines the shortcomings to provide probable solutions to achieve the fabrication of a practical IB-SC.

1.2 Scientific Background

1.2.1 Photovoltaics

The total current-voltage (I-V) characteristics of an ideal diode-like [14] SC under illumination [15] (see Figure 1.1) is a sum of the dark current and the photocurrent. Thus, the total current $I$ can be written as,

$$I = I_s \left[ \exp \left( \frac{qV}{k_B T} \right) - 1 \right] - I_L$$

(1.1)

where, $I_s$ is the diode saturation current, $q$ is the charge and $V$ is the output voltage such that $qV$ is the energy difference between the quasi-fermi levels for electrons and holes, $k_B$ is the Boltzmann constant, $T$ is the temperature of operation, and $I_L$ is the photocurrent generated via solar illumination, which can be obtained by integrating total area under the curve shown in Figure 1.2 (a).

Open circuit voltage $V_{OC}$ can be obtained from 1.1 by equating $I$ to zero,

$$V_{OC} \approx \frac{k_B T}{q} \ln \left( \frac{I_L}{I_S} \right)$$

(1.2)

Thus, at a given $I_L$ the $V_{OC}$ increases logarithmically with decreasing $I_s$, while under ideal conditions $I_s$ decreases exponentially with the band gap. This means that one needs to have large band gap in order to obtain large $V_{OC}$, whereas, large $I_L$ can only be obtained by lowering the band gap (see Figure 1.2 (a)). This imposes a fundamental limit over the output power.
Figure 1.1: Current-voltage characteristics of a SC in dark and under illumination.

The external efficiency, $\eta_{\text{ext}}$ of a SC is given by $P_m/P_{\text{in}}$, where $P_m$ is the maximum power output and $P_{\text{in}}$ is the power input. By properly choosing a load, optimum fraction of the product of $I_{SC}$ and $V_{OC}$ can be extracted (Figure 1.1). Thus $P_m$ is given by,

$$P_m = I_m V_m = FF.V_{OC}.I_{SC}$$

(1.3)

where, $FF = (I_m.V_m)/(I_{SC}.V_{OC})$ is the so-called fill factor, which measures sharpness of the curve and asymptotically approaches to one, with increasing $V_{OC}$.

Finally, $\eta_{\text{ext}}$ can be calculated using following equation,

$$\eta_{\text{ext}} = \frac{V_m^2 I_s(q/k_B T)exp(qV_m/kT)}{P_{\text{in}}}$$

(1.4)

As the dependence of $V_{OC}$ and $I_{SC}$ over the semiconductor band gap is completely opposite to each other, there exists an optimum value of the gap, which will give rise to maximum possible $\eta_{\text{ext}}$. The ideal peak efficiency at $T=300$ K for the solar spectrum given in the inset of Figure 1.2 (b) is about 31% [2, 16]. It can further be increased by using solar concentrators to about 37% - 41% [16, 17] for 1,000 suns.
This increase is primarily due to the increase of $V_{OC}$, while the photocurrent increases linearly with the intensity. Figure 1.2 shows the theoretical efficiency as a function of semiconductor band gap energy. Till date the highest reported (single junction, single-gap SC) efficiency of 28.8% [18, 19] has been obtained for GaAs SC. Thus, in spite being a capable technology, the cost effectiveness of photovoltaic conversion remains a major hurdle in this field.

1.2.2 Intermediate Band Solar Cells -

The Concept

The IB-SC concept proposed by Luque and Marti [13] in 1997 provides a new insight into the conversion efficiencies of SCs, and offers a potential way to increase the limiting efficiency of an ideal single-gap SC from 40.7% [2, 17] to 63.2% [1, 13, 20, 21] under full concentration (Figure 1.3). IB-SCs rely on multi-step-photon absorption with assistance of an engineered IB lying in the mid-gap region of a host semiconductor used as an active material for a SC. Engineering of an IB allows harvesting of photons
with energy below the band gap of the host semiconductor making transitions from the VB to the IB and from the IB to the CB in addition to the conventional VB to CB transitions.

Figure 1.3: (a) A basic structure and working of an IB-SC consisting of an IB material sandwiched between p- and n-type semiconductors; here $E_G$ is the total band gap, whereas $E_L$ and $E_H$ represent the sub-band-gaps. (b) The plot showing limiting efficiency for IB-SC and single-gap SC as a function of $E_H$ and $E_L$; modified after Ref. [21].

In a basic IB-SC [1], a material containing an IB is introduced between conventional p- and n-type semiconductors. This ensures that IB is not in direct contact with external electrodes, and thus only -n and -p type regions act as selective contacts for electrons and holes, respectively. The IB divides the total band gap in two sub-band-gaps as shown in Figure 1.3. Hence, under solar illumination, two-step photon absorption from VB to IB and then IB to CB becomes possible, in addition to the conventional VB to CB absorption. Since the process of inter-band carrier relaxation is much slower than that of the intra-band carrier relaxation, separate quasi-Fermi levels are associated with each of the bands. The output voltage is given by the split between electrons and hole quasi-Fermi levels (see Equation 1.1), thus this voltage is still limited by the total band gap.

In order for IB-SC to work efficiently, there are two essential requirements, first, a completely isolated IB to preserve the voltage and second, a half filled IB in order to optimize two-step photon absorption processes. If this is achieved then the absorption
of additional IB assisted photons will increase the photocurrent substantially, while preserving $V_{OC}$, thus increasing the external efficiency of the cell [1, 13, 21]. Proposed approaches [1, 4] to realize IB-SCs include use of QDs [22–24], bulk semiconductors with impurity doping [25, 26] as well as highly mismatched alloys [27, 28]. There is also a proposal of utilizing transition metals derived from ab initio calculations [1, 29] having appropriate band structure. The formation of the IB by means of QDs is thought to be the most practical and attractive approaches to fabricate an efficient IB-SC [1, 21].

1.2.3 Intermediate Band Solar Cell -

Heterostructures and Quantum Confinement

For fabricating an IB within the band gap of the host semiconductor, band engineering must be done using various heterostructures having appropriate parameters such as band gaps and band offsets. An ability to fabricate these heterostructure in nano-size regime can be exploited to confine charge carriers in a particular region. Generally, semiconductor heterostructures are classified into two categories namely, type-I and type-II (Figure 1.4), depending on the band alignment between the underlying materials. In type-I systems, a narrow band gap material acts as a single potential well for both electrons and holes, thus both the charge carriers are confined

![Figure 1.4](image-url)
in the same material (Figure 1.4 (a)). On the contrary, in type-II systems, the material with the lower potential energy for holes (Figure 1.4 (b)) has the higher energy for electrons and vice versa (Figure 1.4 (c)).

A quantum well is formed by three layers of materials such that the middle layer has the lowest potential for either an electron or a hole or both. A quantum well thus confines electrons or holes or both in a two-dimensional system and hence energy within this well is no longer continuous with respect to the confined direction, usually the growth direction. Energy becomes quantized, although there is a continuum of states joining the confined level and the VB (or CB), associated with the transversal velocity of the electrons (or holes) that is not quantized. As a consequence, quantum well essentially reduces the semiconductor band gap (with respect to that of the barrier material) and therefore produces a new semiconductor with a tunable band gap dependent on the well width [1].

The confinement of carriers can further be extended to one- and zero-dimension, resulting in what are known as quantum wires and QDs [15] (Figure 1.5). QDs create completely confine states within the host band gap, well-separated from the VB maxima or the CB minima and hence can be utilized for IB-SC application. Addi-

![Diagram](image-url)

Figure 1.5: (a) A schematic diagram of a SL structure consisting of vertically aligned type-II QDs separated by a thin host semiconductor. (b) Formation of a miniband within the host band gap for the given SL.
tionally, these nanostructures, separated by barrier regions, can be grown multiple times to form so called superlattice (SL) structures. If the barriers are sufficiently thin, then the wave-functions of the confined charge carriers tend to overlap and consequently discrete energy levels widen to create minibands (Figure 1.5). Formation of a miniband is a desired attribute for an IB-SC in order to enhance below band gap absorption while avoiding the effects of Shockley-Read-Hall non-radiative recombinations (see Section 2.3.1) which get amplified due to presence of localized states [30].

1.2.4 Intermediate Band Solar Cells - Current Status and Challenges

As discussed in Section 1.2.2, there are a variety of possible ways to fabricate an IB-SC. This section briefly describes overall developments in this field of study with the special emphasis on QD based IB-SCs.

Impurity doping was one of the early approaches to fabricate an IB-SC. Although, below band gap absorption was observed in such structures, specifically in ZnTe:O [25] and Si:S [26], no successful efficiency enhancement was observed due to nonradiative recombination channels associated with the isolated impurity states [30]. Thus this approach slowly transformed into a more realistic one which employs highly mismatched alloys (HMAs) as IB materials. HMAs are a class of semiconductors engineered by combining isoelectronic elements with very large differences in terms of atom size, ionicity, and electronegativity [4]. The most studied examples are Ga(N,As) HMAs in which N ions substitute the As sites, as well as Zn(Te,O) HMAs in which O ions substitute the Te sites. These alloys have remarkable optical and electronic properties due to a restructuring of the CB or the VB into multiple subbands as understood in terms of a band anticrossing model [31]. IB-SCs based on HMAs have been grown [27, 28] and the presence of two-step photon absorption processes has also been reported for both GaNAs [32] and ZnTeO [28] HMAs. These results have demonstrated HMAs as potential candidates for SC application, but there are many unresolved issues. The enhancement of photocurrent is still very limited, isolation
of IB is not straightforward and considerable improvement is required in essential device qualities such as charge mobilities and minority carrier lifetimes. Most drawbacks related to HMAs are a result of the inherently large lattice mismatches as well as consequent deterioration of the crystal structure, and thus significant developments are required to address these problems [4].

Another approach apart from the use of QDs is the application of some transition metals derived from ab initio calculations [1, 29]. Optoelectronic properties of novel transition metals have been computed in the hope of finding an ideal IB material [33], but no suitable material has actually been developed. Hence, finding an appropriate material for an IBSC by purely theoretical means is a challenge in itself.

Fabrication of a QD based IB-SC is the most attractive and practical approach. In this case, either electron or hole confinement levels within the QDs can give rise to an IB depending on the band gaps and band offsets of the constituent materials [1, 21]. The proof of concept has been successfully demonstrated in the type-I InAs/GaAs QDs [23, 24, 34] with the IB engineered from the electron confinement levels. Moreover, the efficiencies obtained show improvements as compared to the reference GaAs cell when QDs are appropriately doped [35]. However, there are various constraints that hamper the performance of such IB-SCs [1, 36] as described below:

(i) The band gaps of the prototype InAs/GaAs QD SCs (see inset of Figure 1.6(a)) are far from the theoretically calculated optimal values (Figure 1.3(b)) for host band gap (about 1.95 eV) and the IB (about 0.71 eV) [1, 13, 20, 21]. Some recent progress has been made in order to modify the host band gap and the band offset by growing InGaAs/AlGaAs QDs [37] but further exploration is required to find an ideal material system with appropriate material parameters.

(ii) Most of the reported IB-SCs show an insufficient increase in $I_{SC}$ due to relatively low absorption as a result of the small number of QD containing layers [4]. Only a few layers of QDs can be grown via the Stranski-Krastanov (SK) growth mode. This is a strain driven growth mode (see Section 2.1.3) and the accumulated strain tends to create defects and dislocation after growth of a few QD containing layers, severely damaging the material [38]. Some attempts have been made to grow hundreds of layers of stacked QDs by modifying QD composition (In$_{0.4}$Ga$_{0.6}$As/GaAs QDs [39])
thereby changing the critical thickness. However, this resulted in the thicker wetting layer (WL), another culprit behind the decrease in SC efficiency as will be discussed below. Use of strain compensation method to avoid rapid degradation of the materials has also been attempted [40]. Although, strain compensation improved $I_{SC}$ by improving the crystal quality it also resulted in the reduction of $V_{OC}$ due to the reduction in the band gap.

![Image of degradation and band lineup](image-url)

Figure 1.6: (a) Scanning transmission electron microscopy image showing degradation of material quality due to accumulated strain [38]. Inset: Schematic band line-up of InAs/GaAs system including the effect of the WL [1, 34]. (b) Typical I-V characteristic of an InAs/GaAs QD based IB-SC under illumination compared to a reference GaAs SC [1, 34].

(iii) Existence of the WL formed as a consequence of the SK growth (see Section 2.1.3) reduces $V_{OC}$ as it provides additional states for carrier escape. Application of droplet epitaxy is one of the ways to avoid the formation of WLs [41], but the method is too material specific and the precise control is hard to achieve [42].

(iv) QDs with type-I band alignment have high carrier recombination rates [43, 44] resulting in reduced photocurrent [4]. Furthermore, the situation of having both types of carriers spatially confined in the same volume enhances the probability of electron-hole scattering. As a solution, QD structures with type-II band alignment have been proposed [45–48] and there is a need of exploring novel material systems.

In order to address the above mentioned deficiencies of the InAs/GaAs QDs and
related structures, we have grown and investigated submonolayer type-II ZnTe-rich QDs embedded in a Zn\textsubscript{x}Cd\textsubscript{1-x}Se matrix. The ZnCdSe alloy has a band gap of about 2.1 eV at room temperature [49, 50], when grown lattice matched to InP, hence it can be used as a host material with a band gap close to the ideal value of 1.95 eV. Also, ZnCdTe QDs having a VB offset of about 0.8 eV [51–54] relative to the ZnCdSe can be used to fabricate an IB out of the hole confinement levels, close to the ideal value of 0.7 eV. Moreover, in type-II QDs, the photo-generated electrons and holes immediately separate spatially, and the corresponding wave-functions overlap only via exponential tails reducing the oscillator strength of the electron-hole recombination [55]. This results in longer radiative lifetime and suppression of the non-radiative Auger recombination [56], thereby making the carrier extraction process more efficient in a photovoltaic device. The samples have been grown via a combination of molecular beam epitaxy (MBE) and migration enhanced epitaxy (MEE) and they are being investigated by means of various structural, optical, and electrical characterization techniques.
Chapter 2

Experimental Techniques

2.1 Epitaxial Growth

Semiconductor crystals can be grown layer-by-layer on top of an initial substrate crystal. This method of deposition of a film on a crystalline substrate is termed as epitaxial growth. Epitaxial growth is always preferred as the grown single crystal film has a well-defined orientation with respect to the substrate crystal. The desired film can be grown on the same (homo-epitaxy) or different (hetero-epitaxy) material substrates depending on the availability of the substrate crystal and the structure requirements. Also, epitaxial films may be grown from gaseous or liquid precursors using various methods such as vapor phase epitaxy, liquid phase epitaxy, and MBE.

2.1.1 Molecular Beam Epitaxy

Since its conception in the 1960s, MBE [57, 58] has been at the forefront of basic research related to the study of interfaces, special systems such as heterostructures, SLs and novel alloys, as well as related to the fundamental studies of dopant incorporation and activation. This success of MBE is due to the versatility and simplicity of its operating principle. In MBE, source materials, in elemental form, are evaporated or sublimed from individual effusion cells into an ultra-high vacuum (UHV) chamber and are directed onto the surface of a heated substrate, where they form a crystalline
layer. The evaporated atoms or molecules do not interact with each other until they reach the wafer due to the long mean free paths. One of the major advantages of this technique is that no complex chemical reactions are required to occur at the surface of the substrate which allows analyzing growth processes such as surface migration, three dimensional growth and dopant incorporation. This analysis can be performed in-situ, owing to the UHV environment and the measurements can be used to implement real-time feedback for growth control. Additionally, the molecular and atomic beams can be turned on and off by shutters in front of the cells, which are actuated by computer-controlled motors.

Due to a precise control over growth and due to the ability of fabricating complex yet high-quality structures, MBE has led to the observation of new effects such as two-dimensional transport effects, carrier and photon confinement effects, modulation and delta doping techniques etc. having widespread applications.

2.1.2 Migration Enhanced Epitaxy

In MEE, the constituent elements are supplied alternately in a pulsed mode, to enhance the surface migration of adatoms. Thus, MEE is very useful to grow a high quality atomically flat heterostructures [59] and to reduce defect formation during impurity doping [60]. MEE has also been employed to grow self-assembled QD structures such as CdSe/ZnSe [61, 62], InAs/GaAs [63–65], GaAs/InAs [66], InSb/InAs [67], and ZnTe/ZnSe [68], mostly to avoid the formation of detrimental WLs [65, 69] and to form small QDs, mostly in submonolayer regime.

2.1.3 Growth Mechanisms

The growth of epitaxial films on a single crystal surface depends critically on the interaction strength between adatoms and the surface. In order to fabricate high quality heterostructures, the lattice parameters of the underlying alloys must be matched as this is a physical requirement in atom placement. However, if the heteroepitaxial layer is thin enough, it can physically be strained to the degree that its lattice constant becomes the same as the substrate. Eventually, when the thickness
goes over the critical thickness \( t_c \), misfit dislocations start to appear at the interface and result in permanent electrical defects such as interface traps (QDs can also be formed by releasing built-up strain as discussed later in this section). This is due to the built up strain in the layer which tends to introduce dislocations so as to relax the film (Figure 2.1). Following empirical relation [15] can be used to determine the value \( t_c \), while exact value can be calculated using the theory of dislocation formation,

\[
t_c \approx \frac{a_e}{2\Delta} \approx \frac{a_e^2}{2|a_e - a_s|} \tag{2.1}
\]

where, \( \Delta \) is the lattice mismatch, \( a_e \) and \( a_s \) are the lattice constants of the epitaxial layer and the substrate respectively.

Furthermore, the epitaxial layer grows via a particular growth mode depending on the chemical and physical properties such as surface energies and lattice parameters of the substrate and film. In Volmer-Weber (VW) growth mode (Figure 2.2 (a)), adatom cohesive force is stronger than surface adhesive force, leading to the formation of three-dimensional adatom clusters or nano-islands. On the contrary, during Frank-van der Merwe (FM) growth mode (Figure 2.2 (b)), adatoms attach preferentially to surface sites resulting in atomically smooth, fully formed layers. This layer-by-layer growth is two-dimensional indicating that a complete film forms prior to growth of subsequent layers. The SK growth mode (Figure 2.2 (c)) is an intermediary process in which the growth starts with a formation of two-dimensional layer, however the built-up strain is
released by forming three dimensional nano-islands, generally without the formation of dislocations. Due to its inherent characteristics, the FM growth mode is ideal for growing quantum wells, while QDs can be grown via either VW or SK growth modes. In case of SK grown QDs, a very thin strained layer (WL) remains unbroken which acts as a quantum well and prevents the QDs to form well-separated confined states for electrons (or holes) resulting in a continuum of states following strong IB-to-CB (or VB) thermal escape. Additionally, as this growth mode is primarily a strain driven mechanism, only a few layers of QDs can be grown due to accumulation of strain and subsequent formation of dislocations [38]. Therefore, SK grown QDs pose practical issues while integrating them in an actual device [69–71].

**Experimental Details:** A RIBER 2300P MBE system has been used for the sample growth. The system consists of two separate growth chambers connected by a transfer module under UHV. Elemental In (7N), Ga (7N), As (7N), Be (6N), and Si (7N) are used for the III-V growths in the III-V chamber, whereas elemental Zn (6N), Cd (7N), and Se (6N) and Te (6N) and the nitrogen plasma source are used for the growth of II-VI structures in the II-VI chamber (see Figure 2.3). An essential

![Figure 2.3: Schematic diagram of II-VI MBE chamber.](image-url)
requirement for a MBE system is to attain and maintain UHV inside the chambers as well as the transfer module. This is achieved by means of different pumps connected in series. At first, loading chamber is pumped to about $10^{-4}$ torr using a mechanical roughing pump along with either an adsorption pump or a primary turbo pump. Subsequently a valve to a secondary turbo pump is opened which then pumps down the chamber to about $10^{-9}$ torr. Cryo or ion pumps are used in combination with Ti sublimation pump to preserve UHV conditions in the chamber and the transfer module. Additionally, liquid nitrogen (LN$_2$) cooled cryo-panels are used during the growth to have UHV conditions. In order to maintain UHV at all times, mass spectrometer is used to detect small leaks which are then eliminated immediately.

For the growth, epi-ready substrates are first cleaved carefully and mounted on to clean Mo blocks using In. Mo blocks are cleaned by the process of chemical etching inside a class-100 clean hood. Various chemicals such as de-ionized water, Methanol, Br$_2$:Methanol, hydrochloric acid (HCl), and a combination of HCl and nitric acid (HNO$_3$) (commonly known as aqua-regia) are used along with the ultrasound sonicator. The prepared blocks with the mounted substrate are then placed on the cart and loaded in the loading chamber.

Prior to the growth, a continuous LN$_2$ flow is set up to obtain UHV in all the chambers. The cells and the substrate temperatures are slowly raised and stabilized to the required temperatures and the fluxes of the individual elements are measured using an ion gauge. The substrate temperature is monitored by a thermocouple or a pyrometer and the in-situ growth analysis is performed using reflection high energy electron diffraction (RHEED).

Firstly, oxide desorption of the substrates is performed in the III-V chamber by heating the substrates up to 500°C in case of InP and up to 580°C for GaAs, with an As flux impinging on the surface to prevent metal segregation on surface of the substrate. Then a lattice matched III-V buffer layer is grown and the sample is transferred to the II-VI chamber via transfer module. Prior to the growth of the II-VI epilayers, the sample surface is exposed to a Zn flux, followed by the growth of a II-VI buffer layer at the substrate temperature of 200°C. This step is intended to suppress the formation of Ga$_2$Se$_3$ at the III-V/II-VI interface, which has been shown
to result in the formation of stacking faults [72]. The required structures are then grown at a nominal substrate temperature of 300°C under Se rich conditions using pre-programmed MEE shutter sequences. Specific ratios of beam equivalent pressure (BEP) as shown in Table 2.1 are used to grow various alloys, lattice matched to the substrate. During the MEE cycles, only submonolayer quantities of Te are sequentially deposited between the barriers. Also, the constituent elements are deposited with short pauses in-between, during which all the shutters are turned off. These growth interruptions facilitate enhanced surface migration and assist in the formation of submonolayer QDs embedded in a host matrix. The QDs grow without the formation of a WL analogous to a VW growth mode, and hence hundreds of layers containing QDs can be grown in this growth mode, potentially giving a large number of QDs. An additional advantage of this growth mechanism is that the dopants can be incorporated preferentially into the QDs [68, 73], in order to create a half-filled IB as required for the optimal performance of an IB-SC [20, 24, 35, 41].

<table>
<thead>
<tr>
<th>Epilayer</th>
<th>BEP Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>In_{0.53}Ga_{0.47}As</td>
<td>In/Ga ≈ 2.2 As/(In+Ga) ≈ 50</td>
</tr>
<tr>
<td>Zn_{0.51}Cd_{0.49}Se</td>
<td>Cd/Zn ≈ 2.0 Se/(Zn+Cd) ≈ 4.0</td>
</tr>
<tr>
<td>ZnSe_{0.54}Te_{0.46}</td>
<td>Zn/Te ≈ 1.3 Zn/Se ≈ 1.8</td>
</tr>
</tbody>
</table>

Table 2.1: BEP ratios used for obtaining various alloys lattice matched to InP substrate.
2.2 Structural Characterization

2.2.1 Diffraction

RHEED (see Figure 2.4 (b)) and high resolution x-ray diffraction (HRXRD) are non-destructive analytical techniques which reveal information about the crystal structure, surface configuration, chemical composition and various physical properties of materials.

In kinematical scattering theory [74], constructive interference in the diffraction experiment is determined by the condition that the wavevectors \( k_i \) and \( k_f \) of the incident and diffracted beams respectively, differ by a reciprocal lattice vector \( \mathbf{q} \). When considering only elastic scattering events, that is \( |k_i| = |k_f| \), and the principle of conservation of momentum, this diffraction condition can be cast into the geometrical construction of the Ewald sphere in reciprocal space as shown in (Figure 2.4 (a)). Geometrically, this means that if the origin of reciprocal space is placed at the tip of \( k_i \) then diffraction will occur only for reciprocal lattice points that lie on the surface of the Ewald sphere. Mathematically, this can be represented by Laue equations as follows,

\[
\triangle \mathbf{k} \cdot \mathbf{a} = 2\pi h, \triangle \mathbf{k} \cdot \mathbf{b} = 2\pi k, \triangle \mathbf{k} \cdot \mathbf{c} = 2\pi l
\]

(2.2)

where, \( \mathbf{k} = \mathbf{k}_f - \mathbf{k}_i \) is the scattering vector; \( \mathbf{a}, \mathbf{b} \) and \( \mathbf{c} \) are the primitive vectors of the crystal lattice; and \( h, k \) and \( l \) are the corresponding miller indices.

Reflection High Energy Electron Diffraction

RHEED [74] is a surface-sensitive technique which can be used in-situ for analyzing the growth processes in real time. RHEED describes only a few atomic layers beneath the surface due to the glancing angle of incidence of the electron beam. Lower penetration of the beam implies that the periodic part of the crystal beneath the surface can usually be neglected. Hence, the Ewald’s sphere is similar to that for bulk crystals; however the reciprocal lattice for the sample differs from that of a three-dimensional material. The reciprocal lattices of bulk crystals consist of a set of periodic points in three-dimensional \( \mathbf{k} \)-space, whereas the reciprocal lattice of a crys-
Figure 2.4: (a) Ewald construction showing condition for constructive interference. (b) Side view of RHEED showing formation of intensity maxima at the screen due to intersection of Ewald sphere with reciprocal lattice rods.

d tal surface is a series of infinite rods extending perpendicular to the sample surface due to the lack of a third diffraction condition. Therefore, in case of the RHEED geometry, diffraction conditions are satisfied where these reciprocal rods intersect the Ewald’s sphere as shown in Figure 2.4 (b) and the pattern as well as spacing of the spots provides the information about the reciprocal lattice of the sample surface.

<table>
<thead>
<tr>
<th>Epilayer</th>
<th>Surface Reconstruction</th>
<th>Metal Rich</th>
<th>As or Se/Te rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>(4 × 2)</td>
<td>(2 × 4)</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>(4 × 2)</td>
<td>(2 × 4)</td>
<td></td>
</tr>
<tr>
<td>ZnTe, CdSe, ZnSe</td>
<td>C(2 × 2)</td>
<td>(2 × 1)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: RHEED reconstruction patterns for some materials.

During the growth of an epilayer, a surface reconstruction pattern (see Table 2.2 and Figure 2.5 (a)) develops depending on the evolution of the dimer formations
of the adatoms. The stability of a particular surface configuration depends on the surface energy at a given substrate temperature and the fluxes of the elements in use. Hence, the RHEED pattern is very sensitive in detecting changes in the dimer formation as well as surface modification due to two- or three-dimensional growth modes. Moreover, during layer-by-layer growth (FM growth) in MBE, the surface periodically changes its morphology because of the nucleation and coalescence of islands in the growing layers. This results in the periodic damping and the recovery of RHEED intensity during the growth of each monolayer as shown in Figure 2.5 (b). This phenomenon is known as RHEED oscillations and can be used to determine growth rates, layer thicknesses, and alloy compositions.

![RHEED Intensity](image)

Figure 2.5: (a) Typical (2×1) RHEED reconstruction pattern during the growth of ZnTe epilayer on GaAs. (b) Schematic diagram of the epitaxial surface showing evolution of RHEED intensity at three different growth times ($t_1$, $t_2$, $t_3$).

**High Resolution X-ray Diffraction**

HRXRD has long been used for the characterization of epitaxial layers, particularly for the determination of thickness and composition of the epilayers as well as to evaluate strain and relaxation within a given layer of a multilayer structure. This technique can be simply understood by reducing the Laue equation (Equation 2.2) to Bragg’s law (Equation 2.3).
Bragg’s law gives the condition for coherent and incoherent scattering from the lattice sites in a crystal structure. Bragg diffraction occurs when an electromagnetic radiation with wavelength comparable to atomic spacing is incident upon a crystalline sample. The radiation gets scattered by the underlying atoms and undergoes constructive interference. The path difference between two waves undergoing constructive interference is given by $2d_{hkl} \sin \theta$, where $\theta$ is the scattering angle and $h$, $k$, $l$ are the miller indices of the consecutive crystallographic planes (Figure 2.6). This path difference has to equal to the integer multiple of the wavelength to preserve the phase of incident and scattered waves. Hence, Bragg diffraction condition is given by,

$$2d_{hkl} \sin \theta = n\lambda$$  \hspace{1cm} (2.3)

where, $n$ is an integer, and $\lambda$ is the wavelength of the electromagnetic radiation. HRXRD plot can thus be obtained by measuring the intensity of scattered waves as a function of scattering angle.

![Figure 2.6: Schematic diagram of the Bragg diffraction from a crystalline sample.](image)

Every atom in the unit cell contributes to reflection according to its chemical nature and its relative position. Structure factor, $F_{hkl}$, describes how atomic arrangement influences the intensity as well as the phase of the scattered beam. $F_{hkl}$ is
represented by following relation [75],

\[ F_{hkl} = \sum_{j=1}^{N} f_j e^{2\pi i (h u_j + k v_j + l w_j)} \]  \hspace{1cm} (2.4)

where, \( f_j \) is the atomic form factor of the \( j^{th} \) atom which depends upon the electron charge density about the nucleus and the position of the atom in an unit cell, expressed by coordinates \( u, v, \) and \( w. \) Hence, in a real crystal, presence of many inter-penetrating Bragg planes as well as additional selection rules invoked by the structure factor give rise to rather sharp Bragg peaks at specific scattering angles surrounded by mostly destructive interference, as opposed to the simple structure shown in Figure 2.6. More discussion about the selection rules can be found in Appendix Section A.

Furthermore, a SL structure results in an additional periodicity giving rise to satellite peaks in HRXRD spectrum which can then be used to analyze the thickness as well as structural quality of the grown SL. The SL thickness (\( t_{SL} \)) can be calculated using the Bragg’s law 2.3,

\[ t_{SL} = \frac{\lambda}{\Delta \sin(\theta)} \]  \hspace{1cm} (2.5)

where, \( \Delta \sin(\theta) \) is the average difference between sine of Bragg angles corresponding to the satellite SL peaks. Additionally, small changes in the in-plane and out-of-plane lattice parameters of the epilayers arising due to the strain fields can be detected by measuring \( \omega - 2\theta \) scans in various symmetric as well as asymmetric orientations. As all the samples investigated in this study are grown on (001) oriented substrates, symmetric scans have been performed in (004) as well as (002) orientations and asymmetric scan have been performed in a variety of orientations such as (224), (113) etc. Following expression can be used to calculate lattice spacing, \( d_{hkl} \) for a cubic structure along various orientations,

\[ \frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \]  \hspace{1cm} (2.6)

where, \( a \) and \( b \) are the in-plane lattice parameters of the epilayer, whereas \( c \) is the average lattice parameter along the growth direction. Thus, \( c \) can be calculated directly from the Bragg peak along (004) reflection using Bragg’s law (Equation 2.3)
and assuming that the cubical unit cell is deformed to tetragonal due to equal biaxial in-plane strain components, i.e. \( a = b \neq c \). Hence, the inter-planar spacing for a tetragonal unit cell of this kind is a function of \( a \) and \( c \) only. With the known value of \( c \), the average in-plane lattice parameter can be calculated, for example, from the Bragg peak along the (224) reflection using the following formula,

\[
a^2 = \frac{8}{(1/d_{224}^2 - 1/d_{004}^2)}
\]

where, \( d_{224} \) and \( d_{004} \) are the lattice parameters obtained from \( \omega - 2\theta \) curves along (224) and (004) reflections respectively, using the Bragg’s law.

Additionally, to confirm the calculated parameters of the multilayer structures obtained from HRXRD experiments, \( \omega - 2\theta \) curves can be simulated. In this study, a commercially available BEDE RADS program based on Takagi [76] and Taupin [77] generalized dynamical theory has been used for this purpose. Initial parameters required for the simulation such as spacer compositions, thicknesses and strain were obtained from various symmetric and asymmetric HRXRD scans and the QD array was replaced by an effective layer with the same structure factor as that of the QDs.

**High Resolution X-ray Diffraction based Reciprocal Space Mapping**

**Out-of-plane Reciprocal Space Map:** Conventional \( \omega - 2\theta \) scans are geometrically equivalent to \( q_z \) scans at \( q_x = 0 \), where \( q_z \) and \( q_x \) are the \( z \)- and \( x \)- components of momentum transfer between incident and scattered wave vectors (Figure 2.7 (a)) and are useful for extracting the information such as lattice mismatches, compositional changes and strain in the layers, as discussed in the previous section. Whereas HRXRD based reciprocal space maps (RSMs) provide information about diffuse scattering due to impurities, dislocations and QDs embedded in the host material. During RSM studies, various \( \omega - 2\theta \) scans are carried out by offsetting \( \omega \) by a small angle \( (\Delta\theta) \), in order to probe along non-zero values of \( q_x \) (Figure 2.7 (b)).

Self-assembled QDs give rise to diffuse x-ray scattering accompanied by the coherent diffraction from the whole sample [78] due to the difference in the scattering factors and the elastic deformation field in the matrix surrounding the dots, which tends to orient the dots in a particular way. Also, any symmetry in QD positions
along $x$-$y$-plane in a real space translates into an elongated SL peak along $q_z$, while any correlation along $z$-coordinate in real space translates into an elongated SL peak along $q_x$, due to fundamental nature of the two spaces. Figure 2.7 (c)-(f) shows schematic RSMs for various possible conditions. A theoretical description based on a statistical kinematical approach showed that the diffuse scattering around the coherent SL peaks gets elongated along $q_x$ and consequently the width of the diffuse maximum in the $q_z$ direction gets relatively narrower if the QDs are vertically correlated [78]. The vertical QD alignment is supposed to give rise to the uniformity in QD size, improving the structural quality and consequently overall IB-SC performance [79]. Additionally, the vertical correlation (as discussed in section 1.2.3) is important in order to ensure a sufficient overlap of the QD confined hole wave functions to facilitate the miniband formation [80, 81] within the band gap of the host semiconductor, which is an advantageous feature for successful operation of an IB-SC.

In order to estimate the degree of QD vertical correlation a theoretical model formulated by Kegel et al. [82] has been used. In this model a Gaussian distribution of horizontal deviations from the underlying reference dot is assumed. The concept
of a mean stacking fault \( \sigma \) has been developed which is a standard deviation in the lateral QD position and hence essentially captures the average quality of the vertical dot alignment. Also, the form factor and the transmission functions have been neglected as they exhibit a slow variation along \( q_z \) and only provide for a monotonous background. Therefore, the value of \( \sigma \) can be estimated from half width half maxima (HWHM) along \( q_z \) using following relation,

\[
q_z^{HWHM} = \frac{1}{D} \text{arccosech}(\sigma^2 q_z^2 + \mu) 
\]

(2.8)

where, \( D \) is the SL period, and \( \mu \) is the attenuation factor related to the loss of intensity in the x-ray beam from one SL layer to the next. An approximation of above equation can be made which deviates from the exact expression by less than 1\% for \( \sigma q_x < 0.5 \).

\[
q_z^{HWHM} = \frac{\sigma^2}{D} q_z^2 + \frac{\mu}{D} 
\]

(2.9)

Using equation 2.9 relative stacking fault \( f_s \) i.e. relative lateral deviation from one dot to the next can be estimated to be:

\[
f_s = \frac{\sigma}{2r} \sqrt{\frac{2}{\pi}} \left( 2 - \frac{\sigma}{2r} \sqrt{\frac{2}{\pi}} \right) 
\]

(2.10)

where, \( r \) is the radius of the QDs.

\[ \text{In-plane Reciprocal Space Map:} \]

In-plane RSM is required to investigate morphology of the QDs along the plane of the sample surface. In-plane diffuse scattering corresponds to the average ensemble of illuminated dots and is sensitive to dot shape and size distribution. Figure 2.8 shows a schematic diagram of a typical HRXRD set-up required for recording \( \omega - \phi \) scans.

To explain the experimental observations, in-plane diffuse scattering can be computed as follows. The total intensity is approximated as an incoherent sum of individual diffraction pattern:

\[
I(\vec{q}) = \sum_{\text{Distri}} I_{QD}(\vec{q}) 
\]

(2.11)

where \( I_{QD}(\vec{q}) = | \sum_j f_j(q) e^{i\vec{q}\vec{r}_j} | \) is the diffraction signal from an individual QD. Thus, a specific model taking into account realistic QD shape and dispersion can be developed.
Figure 2.8: Schematic diagram of a typical experimental set-up used for performing \(\omega - \phi\) scan.

**Experimental Details:** HRXRD measurements were performed at the City College of New York, CUNY, using a Bruker D8 Discover x-ray diffractometer with a Cu source (\(\lambda = 1.54056\) Å).

Detailed HRXRD measurements including RSMs were carried out at Beamline X20A at the National Synchrotron Light Source at the Brookhaven National Laboratory. All measurements were performed using monochromatic synchrotron radiation either at 8 or at 9.2 keV, with a double-crystal Ge (111) monochromator. To enhance the angular resolution, a Ge (111) analyzer was placed in front of the detector.

### 2.2.2 Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry (SIMS) is a tool to analyze the composition of a sample and can provide elemental depth profiles over a depth range from a few angstroms (Å) to tens of microns (\(\mu m\)) (Figure 2.9). In this technique, the surface of the specimen is sputtered with a focused primary ion beam (usually O or Cs). Various electrostatic lenses and apertures control the intensity and shape of the primary beam. Secondary ions formed during this process are immediately removed by an extraction,
or immersion lens. These secondary ions are then transferred by a second electrostatic (transfer) lens into a mass spectrometer (usually a quadrupole or magnetic sector) in order to determine the composition.

**Experimental Details:** SIMS measurements on the investigated samples were performed by EVANS Analytical Group at their lab in Sunnyvale, CA.

### 2.2.3 Electron Microscopy

An electron microscope is a type of microscope that uses a beam of accelerated electrons as a source of illumination to create an image of the specimen. As the DeBroglie wavelength associated with these electrons is much smaller than the visible light, it is capable of much higher magnifications and has a greater resolving power than an optical microscope allowing it to see much smaller objects in finer detail.

All electron microscopes use electromagnetic and/or electrostatic lenses to control the path of electrons. The basic design of an electromagnetic lens is a solenoid through which one can pass a current, thereby inducing an electromagnetic field. The electron
beam passes through the center of such solenoids on its way down the column of the electron microscope towards the sample.

Following sections briefly discuss a few standard types of electron microscopes.

**Scanning Electron Microscopy**

The Scanning Electron Microscope (SEM) produces images by detecting secondary electrons which are emitted from the surface due to excitation by the primary electron beam (Figure 2.10). The secondary electrons are first collected by attracting them towards an electrically biased grid and then further accelerated towards a scintillator-photomultiplier system. The electron beam is scanned across the surface of the sample in a raster pattern, with detectors building up an image by mapping the detected
signals with beam position. Because the SEM image relies on electron interactions at the surface rather than transmission it is able to image bulk samples and has a much greater depth of view, and so can produce images that are a good representation of the three-dimensional structure of the sample. Modern SEMs are generally capable of producing accelerating voltages up to 30 kV with a resolution as low as 1 nm.

**Transmission Electron Microscopy**

Unlike the SEM, in transmission electron microscope (TEM) the electrons in the primary beam are transmitted through the sample. TEM involves a high voltage (typically 100-400 kV) electron beam emitted by a cathode, which is then transmitted through a very thin specimen. The beam is then magnified by a series of magnetic lenses until it is recorded by a detector such as a charge-coupled device camera. The transmitted electron beam carries information about the structure of the specimen. At smaller magnifications, TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, and allow for the observation of modulations in chemical identity, crystal orientation, electronic structure. Development the field emission gun and adding a high quality objective lens has led to the improved design of so called scanning transmission electron microscope (STEM). STEM is distinguished from conventional TEM by focusing the electron beam into a narrow spot which can be scanned over the sample in a raster pattern. The rastering of the beam across the sample makes these microscopes suitable for analysis techniques such as mapping by energy dispersive x-ray (EDX) spectroscopy and and high angular annular dark-field imaging (HAADF). By using a STEM and a HAADF detector, it is possible to form atomic resolution images where the contrast is directly related to the atomic number (z-contrast image). Hence, these techniques can be employed for high resolution characterization of multilayered structure, interfaces, dislocations and grain boundaries etc.

**Experimental Details:** The SEM analysis was performed at the City College of New York, CUNY, using Zeiss Supra 55 field emission SEM. The TEM analysis was
2.3 Optical Characterization

2.3.1 Photoluminescence

Photoluminescence spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. The carriers within the sample are photoexcited using a laser light and the light emitted upon the relaxation is then collected and analyzed using a spectrometer. The energy of the emitted light is related to the difference in energy levels between the two states involved in the transition.

More specifically, a detailed information about the excitonic properties can be extracted from PL measurements. An exciton is a quasi-particle consisting of an electron and a hole (created via photo-excitation in this case) bound together due to attractive coulomb force. If the electron and hole are separated over many lattice constants (which is generally the case), i.e. if the exciton wavefunction is strongly delocalized and the exciton can move freely inside the crystal, then such a quasi-particle is also called a free exciton. Defects within the semiconductor band gap can trap excitons, essentially localizing them. Such excitons are known as bound excitons. Thus, the annihilation of different excitons (i.e. radiative recombination) is accompanied by a characteristic luminescence and provides information unique to that particular exciton.

Apart from radiative recombination process, there are various ways in which an electron hole pair can recombine non-radiatively. The most important non-radiative recombination mechanisms are:

(i) Recombination through defects or Shockley-Read-Hall (SRH) recombination: This is a two-step recombination process, in which one of the charge carriers gets trapped at the defect and the other carrier move up to the same energy state and recombines non-radiatively.

(ii) Auger recombination: Auger Recombination involves three carriers. An electron and a hole recombine, but rather than releasing the energy as heat or as a photon,
the energy is given to a third carrier.

Non-radiative recombination processes tend to dominate at higher temperatures due to enhancement in the phonon mediated interactions and depend on the crystalline quality of the sample apart from the direct/indirect nature of the semiconductor material. Hence, low temperatures are generally suitable to infer about radiative recombination processes via PL.

Furthermore, internal or external strain (see Appendix Section C), electric as well as magnetic fields can significantly modify the excitonic structure. Additionally, the strength of interaction of charge carriers with longitudinal optical (LO) phonons can also be determined by systematic investigation of PL line-widths as a function of temperature [83]. Hence, PL analysis provides crucial insights into the band structure of the material, and as a result, it has also been an important technique for measuring the purity and crystalline quality of semiconductors and for quantification of the amount of disorder present in a system.

**Type-II Heterostructures - Steady State Photoluminescence**

As discussed in section 1.2.3, in type-II QDs, the photo-generated electrons and holes separate spatially, hence inducing an electric field at the interface of the heterojunction, which results in carrier density dependent band bending [84–88] (Figure 2.11). Thus, a strong blue shift in the PL emission energy is observed due to narrowing of the quantum well formed at the QD-barrier interface at higher excitation intensities and the PL peak positions approximately follow the cube root dependence on the excitation intensities [85, 87].

**Type-II Heterostructures - Time-resolved Photoluminescence**

Time-resolved PL (TRPL) technique can be employed to investigate radiative recombination dynamics and the radiative recombination lifetime can be estimated, which is a measure of electron-hole wavefunction overlap within the structure. This can be achieved by exciting the sample with a pulsed laser and collecting the luminescence as a function of time. In case of type-II nanostructures, the radiative
recombination lifetime decreases with increase in excitation intensity due to enlarged electron-hole wavefunction overlap as a result of the enhanced electric field at the interface [83–85, 88]. Therefore, excitation intensity dependent behavior of both PL and TRPL spectra is a characteristic feature of type-II nanostructures.

**Type-II Heterostructures - Magneto-photoluminescence**

As mentioned in Section 2.3.1, external magnetic field affects the electronic structure, consequently affecting the PL. Conventional magnetic field dependent effects include zeeman splitting [89] and diamagnetic shifts [90], however we use magneto-PL to study subtle quantum mechanical effects peculiar to type-II QDs. Vertical correlation (Section 3.4) in these submonolayer QDs separated by a thin spacer causes them to form vertical stacks [91] resulting in a cylindrically symmetric type-II QD structure (see Figure 2.12 (a)), a favorable geometry for an observation of excitonic Aharanov-Bohm (A-B) effect [55]. In the presence of external magnetic field applied in a Faraday geometry, the angular momentum of a type-II exciton makes a discrete
transition from a zero to a non-zero angular momentum state [92–95]. This transition from a bright to a dark excitonic state changes the PL intensity due to optical selection rules [55, 95]. The magnetic field value, $B_{AB}$ of the AB transition is dependent on the trajectories of electrons and holes and the following equation can be used to calculate electron ($R_e$) and hole ($R_h$) radii as discussed in Ref. [96, 97].

\[
\frac{\hbar^2}{2} \left( \frac{m_e R_e^2 + m_h R_h^2}{R_0^2} \right) R_0^2 \left( \frac{\phi}{\phi_0} \right)^2 = \frac{\hbar^2}{2} \left( \frac{m_e R_e^2 + m_h R_h^2}{R_0^2} \right) R_0^2 \left( -1 + \frac{\phi}{\phi_0} \right)^2
\] (2.12)

$$\implies \phi = \left( \frac{\phi_0}{2} \right)$$ (2.13)

where, $R_0 = (R_e + R_h)/2$, $\phi = \pi(R_e^2 - R_h^2)B_{AB}$, and $\phi_0 = \hbar/e$ is the flux quantum. As an example, in Figure 2.12 (b) the integrated PL intensity of all the samples are plotted as a function of the magnetic field, $B_{AB}$ for each of the curve is related to the average radial size of the QDs in the corresponding sample.

**Experimental Details:** PL and TRPL measurements were performed using either a Janis Research or an Advanced Research Systems closed cycle refrigerating system. For PL studies, the 351 nm emission line from an Ar$^+$ laser was used as an excitation source, while TRPL measurements were performed using the 337 nm line of a N$_2$ pulsed laser with 4 ns pulse width. The excitation intensity was varied by over four orders of magnitude using neutral density filters. The signal was dispersed through a third stage of a TriVista SP2 500i triple monochromator and was detected by a thermoelectrically cooled charge coupled device (CCD) camera or a thermoelectrically cooled GaAs photomultiplier tube. The TRPL signal was recorded using a 500 MHz Tektronix TDS 654C oscilloscope.

Magneto-PL was performed using either a 9 T superconducting magnet at Queens College of CUNY or an 18 T superconducting magnet at National High Magnetic Field Laboratory. Both the magnets were outfitted with a fiber optic probe, used to excite and collect the PL. The detection for the magneto-PL experiments was done by an Ocean Optics HR4000 solid state spectrometer.
Figure 2.12: (a) Schematic diagram of stacked type-II ZnTe/ZnSe QDs in presence of external magnetic field, applied along the growth direction; schematic band line-up of the heterostructure is also represented on the top. (b) Magneto-PL spectra of several samples listed in Table 3.1 showing A-B oscillation.

2.3.2 Absorption Spectroscopy

Absorption spectroscopy is a technique that measure the absorption of radiation, as a function of frequency or wavelength. The absorption spectrum depends on the interaction of the radiation with the sample and thus reveals information about material properties, specifically the band structure. We have used this technique to estimate the band edges of the studied semiconductors and to investigate the below band gap absorption. This section briefly discusses the technique, employed in case of samples under investigation. Optical absorbance, $A$, can be calculated by collecting the transmitted light from the sample. The absorption coefficient, $\alpha$ is then calculated using $A$, and the thickness of the sample, $t$, using the following equation [98]:

$$\alpha = 2.303 \left( \frac{A}{t} \right)$$

Following empirical relation can then be used to estimate the band edge of the
\[ \alpha h\nu = B \sqrt{E_G - h\nu} \]  

(2.15)

where, \( B \) is a constant, \( h\nu \) is the photon energy, and \( E_G \) is the barrier band edge.

**Experimental Details:** For absorption measurements, samples were glued to a glass slide using optical epoxy and the substrates were then mechanically polished. After thinning the substrate to about 50 \( \mu m \), chemical etching was done for the complete removal of the InP substrate and InGaAs buffer layer. A solution of HCl and phosphoric acid (H\(_3\)PO\(_4\)) in the ratio of 6:1 was used for etching InP, whereas a solution of hydrogen peroxide (H\(_2\)O\(_2\)), H\(_3\)PO\(_4\) and de-ionized (DI) water in the ratio of 1:1:6 was used for etching InGaAs [99]. The absorption measurements were done in an ARC closed cycle refrigerating system from 10 K to room temperature. A broad spectrum halogen lamp was used as a light source and the signal was collected using an Ocean Optics VIS-NIR spectrometer.

### 2.4 Electrical Characterization

Excellent electrical properties are essential to achieve high efficiencies in case of all working devices. Therefore, it is required to obtain optimized carrier concentrations with adequate carrier mobilities in order to fabricate a p-i-n structure. Hence, Hall measurements were performed to analyze the electrical properties of the investigated doped samples.

#### 2.4.1 Hall Measurement

The basic working principle underlying the Hall effect measurement is the Lorentz force,

\[ \mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \]  

(2.16)

where, \( \mathbf{v} \) is the velocity of the moving charge \( q \), and \( \mathbf{E} \) and \( \mathbf{B} \) are the external electric as well as magnetic field respectively.
If we apply external magnetic field perpendicular to the sample surface and if a constant current flows through two peripheral ohmic contacts as shown in Figure 2.13 (b), then electrons (for an n-type semiconductor) subject to the Lorentz force, drift towards the other two corners producing a potential drop. The magnitude of this transverse voltage (or Hall voltage, $V_H$) can be extracted using following relation,

$$|V_H| = \frac{IB}{qn_S} \quad (2.17)$$

where $I$ is the current, $B$ is the external magnetic field, $q$ is the charge ($1.602 \times 10^{-19}$ C), and $n_S$ is the sheet density. Since sheet resistance depends on both sheet density and mobility, if sheet resistance ($R_S$) is known, then one can determine the Hall mobility ($\mu$) using the equation,

$$\mu = \frac{|V_H|}{R_SI_B} \quad (2.18)$$

Figure 2.13: (a) Schematic diagram of four probe resistivity measurement using van der Pauw technique. (b) Schematic diagram of Hall measurement technique.

The sheet resistance, $R_S$, of the semiconductor can be determined using the van der Pauw resistivity measurement technique as shown in Figure 2.13 (a).

**Experimental Details:** The Hall measurements were performed at the City College of New York, CUNY, using Lakeshore Hall measurement system.
Chapter 3

Results and Discussion

3.1 Growth Optimization of Type-II ZnTe/ZnSe Quantum Dots

3.1.1 Controlling Size and Density of Quantum Dots via Migration Enhanced Epitaxy

For practical applications of the QDs, it is essential to control their sizes and distribution; parameters that remain elusive in many cases. Initial studies were performed on type-II ZnTe/ZnSe QDs in order to obtain ideal growth conditions. A specific shutter sequence shown in Figure 3.1 (a) was used to grow these multilayer structures with a spacer thickness of less than or equal to 10 monolayers (see Figure 3.1 (b)). This material system was then modified to obtain ZnCdTe QDs embedded in ZnCdSe, an ideal system for IB-SC application.

Submonolayer QDs are difficult to image due to the low electron density contrast between the QD forming material and the host matrix. Thus, quantitative structural information cannot be obtained via TEM analysis. Light layers in HAADF-STEM image shown in Figure 3.2 correspond to Te-rich regions and a nominal SL period can also be observed. But even high resolution techniques such as HAADF-STEM are unable to image the submonolayer QDs. Therefore, we use a variety of charac-
Figure 3.1: (a) A typical shutter sequence used during the growth of ZnTe/ZnSe QD sample with three Te MEE cycles. (b) A schematic diagram of a multilayered structure consisting of ZnTe-rich submonolayer QDs embedded in ZnSe grown on GaAs substrate; here Z denotes the growth direction.

The structural characterization was performed using HRXRD measurements (Figure 3.3) in order to calculate strain and compositions in each of the samples. The out-of-plane and in-plane lattice parameters for the SLs were calculated by performing $\omega - 2\theta$ scans along (004) and (224) orientations respectively and using Bragg's law as discussed in Section 2.2.1. Consequently, these lattice parameters allowed us to calculate average strain and compositions; the results obtained are shown in Table 3.1. Weak satellite SL peaks were also observed in the HRXRD scans as shown in Figure 3.3, which were then used to calculate the SL period.

This analysis also led us to confirm a rather interesting observation that in these samples, MEE and consequently the formation of submonolayer QDs suppressed rapid relaxation that usually occurs due to the natural lattice mismatch between the GaAs substrate and the ZnSe matrix. The strain calculated from HRXRD measurements was plotted with respect to the sample thickness (Figure 3.4) for the samples with
very low Te concentrations (samples A through E). This allowed estimation of the critical thickness of ZnSe with a slight inclusion of Te grown on GaAs. This value was estimated to be $\sim 225$ nm, considerably larger than the previously reported values ($\sim 100$ to $150$ nm) for bulk ZnSe on GaAs \cite{101, 102}. MEE has been shown to be very useful to grow high quality atomically flat heterostructures \cite{59} as well as to grow QDs with enhanced size uniformity \cite{65, 103} due to the enhancement in the surface migration of adatoms. Here, we have applied this technique to grow self-assembled submonolayer QDs. This growth process results in the formation of QDs essentially without the formation of WLs, analogous to the so called VW growth mode. The results show that the formation of submonolayer QDs via MEE leads to high structural quality of the samples.

SIMS analysis was performed on all the samples to measure average Te concentration and the results are shown in Figure 3.5. Although Te was only incorporated in the QD regions, the SIMS analysis does not spatially resolve the thin spacer regions ($<10$ monolayers), and an approximately flat Te concentration trace, indicative of the value of the average Te concentration within the structure, is obtained. The SIMS data was also used to calculate the composition of the SL structures by using the
known values of volumetric atomic densities of ZnTe and ZnSe. The Te concentration values as well as the percentage of Te content for each sample are summarized in Table 3.1. The results show that if the spacer thickness is kept constant, Te concentration in the samples increases with Te cell temperature and with the number of Te cycles. To further examine the effect of varying growth conditions on the formation of the type-II QD structures, a new parameter $\tau$ was introduced, which is a better measure of actual Te content in the samples [100].

$$\tau = Flux_{Te} \times MEE_{Te}$$  \hspace{1cm} (3.1) 

where, $Flux_{Te}$ is the actual Te flux (BEP) measured prior to the growth of the sample and $MEE_{Te}$ is the time for which Te shutters were kept open during an MEE shutter sequence (Table 3.1).

The optical characterization was done by performing PL as well as magneto-PL experiments at 10 K. The normalized PL spectra at 10 K for all the samples are shown in Figure 3.6 (a). The PL spectra, consistent with our previous reports, are typically broadband consisting of a blue band (BB) (>2.7 eV) which is attributed mostly to the emission from Te isoelectronic centers (ICs) in ZnSe spacers and a blue band (GB) (<2.7 eV) that originates from the QD-related emissions [84]. Near band-edge sharp emission lines are observed in the PL spectra of samples with lowest Te content (samples A and B) which are known to be due to small concentration of ICs in the spacer regions. Presence of up to four phonon replicas also point toward a
Table 3.1: Important parameters of the samples under investigation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te flux in $10^{-7}$ torr</td>
<td>0.40</td>
<td>0.24</td>
<td>0.26</td>
<td>0.38</td>
<td>0.40</td>
<td>1.60</td>
</tr>
<tr>
<td>Number of Te MEE cycles</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$\tau$ in $10^{-7}$ torr.s</td>
<td>2</td>
<td>3.6</td>
<td>3.9</td>
<td>5.7</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>SL period in nm</td>
<td>1.7</td>
<td>2.5</td>
<td>1.7</td>
<td>2.5</td>
<td>1.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Number of periods</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>250</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>Te content from SIMS (XRD) in %</td>
<td>0.1 (-)</td>
<td>0.2 (-)</td>
<td>0.3 (0.1)</td>
<td>0.3 (0.2)</td>
<td>0.5 (0.3)</td>
<td>3.2 (2.6)</td>
</tr>
</tbody>
</table>

large electron-phonon interaction. Thus, in spite of some distribution in QD sizes, the biggest contributor to the broad PL line widths is the electron-phonon interaction, as in bulk ZnSeTe, due to the hole trapping at Te ICs [104] (similar results have been obtained for ZnMgTe/ZnSe QDs [83]).

Firstly, excitation intensity dependent PL analysis was performed to confirm the presence of type-II band alignment (not shown here). We observed the expected blue shift in PL peak position with an increase in excitation intensity for all the samples [97], which is a signature of type-II behavior [84, 86].

For detailed spectral analysis of the PL data, the spectra were fitted with four Gaussian lineshapes (Figure 3.6 (a)). The near band edge BB mostly originates from the emission from Te ICs, while the contribution from QDs dominates in all the other GBs as discussed earlier in this section. It is observed that as $\tau$ increases, the contribution from the GBs goes up with a small red shift in PL peak positions (Figure 3.6 (b)), indicating rise in QD density along with a slight increase in QD dimensions with $\tau$. Thus, the peak positions of all the three GBs associated with the QD emissions were used to estimate the average QD size, specifically the thickness, by simply solving 1-dimensional Schrödinger equation. Note that there is a considerably
Figure 3.4: A plot of strain calculated from HRXRD analysis as a function of sample thickness for samples with low Te content.

Figure 3.5: SIMS data for all the samples showing average Te concentration as a function of depth.

large electron-phonon interaction accounting for most of the width of these lineshapes as discussed earlier whereas the contribution to the confinement due to radial dot sizes is negligible as will be discussed in the following sections. Figure 3.7 (a) shows the band alignment in this heterostructure while Figure 3.7 (b) shows the dependence of heavy hole and light hole confinement energies on various QD thicknesses, both calculated using previously reported parameters [53, 105].

We have used Magneto-PL to obtain an accurate estimation of the radial sizes of the submonolayer QDs as discussed in Section 2.3.1. The average QD radii for the samples in this study are estimated to be about 13 to 20 nm, justifying the claim that most of the confinement in these disc-shaped QDs is along the growth direction i.e. due to the QD thicknesses.

Moreover, accurate estimates of the distributions of QD radii can be obtained with the help of high resolution spectral analysis of the magneto-PL spectra [96, 106]. Through this analysis, it was observed that the lateral QD size changes more or less discretely and is related to the average lateral size of the stack of the QDs. The combined result of the calculated QD thicknesses and radii over the complete PL spectrum is shown in Figure 3.8. The discrete changes in the lateral QD sizes appear to coincide with the specific energy values where different lineshapes start to
Figure 3.6: (a) PL spectra of all the samples at 10 K along with the fitted Gaussian lineshapes. (b) The change in the peak position as a function of $\tau$ for each of the line shapes.

overlap each other. Furthermore, sample F shows continuous change in QD radii with relatively large lateral size dispersion as indicated by the observation of a broad peak in magneto-PL spectrum, whereas, the QD radius in sample A does not vary over the entire PL spectrum resulting in a very narrow peak in magneto-PL spectrum [106].

Upon obtaining the spectral distribution of QD radii and the thicknesses, the ratios of normalized the intensities of the GBs were used as indirect probe of the QD distribution in various spectral reions. Therefore, these ratios were then utilized to estimate weighted QD volume distribution over the full PL spectrum for each of the sample (Figure 3.9).

The density of QDs ((Figure 3.10) (b)) was then estimated from this calculated QD volume as follows. Considering that all the Te is concentrated within the QDs, the areal density of QDs, $n_{QD}$, can be calculated as:

$$n_{QD} = \frac{N_{SIMS}}{N_{Te}} \left( \frac{L}{V_{QD}} \right)$$  \hspace{1cm} (3.2)

where $N_{SIMS}$ is the average Te concentration provided by the SIMS measurements, $N_{Te}$ is the volumetric atomic density of Te in Zn(Se)Te QDs, $V_{QD}$ is the average volume of the QDs, and $L$ is the average superlattice period obtained from HRXRD as well as from SIMS (Table 3.1). We plot average QD radii and thicknesses ((Fig-
Figure 3.7: (a) Schematic band line-up of ZnSe$_{0.3}$Te$_{0.7}$/ZnSe QD system. (b) Calculated hole energy levels inside the submonolayer QDs as a function of their thicknesses (ML denotes thickness of a single ZnSe$_{0.3}$Te$_{0.7}$ monolayer); here, HH and LH correspond to heavy and light holes respectively. Also, subscripts 1 and 2 ground and first excited states, respectively.

Two important conclusions are reached. First, we note that concentrations at least one order of magnitude higher would be required to form a full ZnTe-rich monolayer (i.e. for the QDs to physically coalesce into a continuous layer). In this investigation, during each MEE cycle, the amount of Te is supplied in such a way that there is less than a monolayer of ZnTe formed, i.e. less than is needed to form a wetting layer. Thus, no wetting layer forms in this regime and such a growth mode is analogous to VW growth. Although this is not surprising from the growth perspective, we make
Figure 3.8: Combined diagram of the spectral dependence of QD radii and thicknesses overlaid on the corresponding PL spectra, the GBs are specifically highlighted to stress the fact that that QD-related emissions dominate in those spectral regions.

a special note of this as, for certain applications of QD structures, the absence of a wetting layer is critical.

Second, the observed dependence of average QD size and density as a function of Te flux as well as number of Te MEE cycles shows that these are the key parameters to control QD dimensions and distribution. The other variables such as the substrate temperature as well as the interruption time during the MEE cycles may introduce more subtle changes in the formation mechanism of the QDs. Effect of some of these variables have been studied before [107] and all such parameters were essentially kept constant in this set of samples.

The data also appears to indicate that the thickness of these QDs starts to vary prior to the variation in the lateral QD size (Figure 3.8). Sample A has a sharp AB peak in the magneto-PL spectrum and position of which shows no change when we
Figure 3.9: A plot showing spectrally resolved, normalized weighted QD volume as a function of PL energy, overlaid with the PL spectra of individual samples.

perform the spectral analysis, indicating the presence of dots with almost zero lateral size variation. Nonetheless, there is a significant thickness distribution in this sample. Also, sample F with comparatively larger QDs shows only about 20% variation in the dot radius with the lowest thickness distribution. This is most probably due to the stacked nature of the QDs as the vertical QD correlation is supposed to enhance QD size uniformity [91]. This also leads to the observation of a small increase in the radial dot size (~46%) as opposed to about 150% increase in the average QD thickness as values of $\tau$ vary from sample A through F. Moreover, the increase in density from sample A through F is about 670%, much larger than that of the QD size.
3.1.2 Quantum Dot Shape Anisotropy Probed using High Resolution X-ray Diffraction

It is difficult to quantify and to control morphology and size dispersion of embedded ultra-small features such as self-assembled semiconductor QDs. Specifically, submonolayer QDs [63, 108] remain less explored due to much lower electron density contrast with regard to the host material (as discussed in Section 3.1) as well as due to their significantly small dimensions. QDs, grown via SK growth mode [109, 110], are relatively larger and have well defined boundaries. These properties definitely aid imaging these structures using electron microscopy techniques, whereas imaging embedded submonolayer QDs is still a major challenge. Moreover, implementation of practical devices requires detail understandings of the QD morphology, the mechanism of strain relief and defect formation.

Various HRXRD based RSM studies [78, 82, 111–113] have been carried out previously to characterize vertical as well as lateral self-ordering of SK grown QDs, but most of them also involve assistance from some direct imaging technique. A few HRXRD studies related to submonolayer QDs have been reported [64, 91] but a comprehensive structural analysis appears elusive. We have developed and employed a
In this section we discuss the utilization of both, experimental as well as simulated HRXRD based in-plane RSM to reveal preferential elongation of submonolayer QDs. We make use of unique magneto-PL signal obtained from these type-II structures to extract QD size dispersion, one of the important input parameters required for the HRXRD simulations. We also support the findings by performing linear polarization dependent PL experiment and conclude that this indirect collective characterization technique is the best way to understand structural properties, in particular morphology of these hard-to-image submonolayer QD structures. Additionally, non-destructive ways requiring minimal sample preparation are always desirable for structural analysis and thus this composite technique, in principle, provides a way to investigate ensemble of embedded ultra-small structures.

Initially, several $\omega - 2\theta$ scans were performed along symmetric as well as asymmetric orientations to characterize basic structural properties of the SL such as periodicity, roughness and average composition. Then conventional $q_x - q_z$ RSMs were collected to acquire out-of-plane information as described in Ref. [78, 82, 91, 111, 113, 114]. QD morphology has been deduced from diffuse scattering data obtained by measuring in-plane RSM as described in Section 2.2.1. Specific trajectories in reciprocal space have been recorded to measure in-plane map around (004) SL(-1) peak. A set of rocking curves, collected individually around SL(-1) peak (from 0° to 360°) has been merged to obtain a proper $q_x - q_y$ map as shown in Figure 3.11(a). SL(-1) peak was specifically chosen for this analysis as it is well separated from both the substrate as well as ZnSe buffer layer Bragg peaks but still has high enough signal strength to obtain reliable data. Also, satellite peaks exhibit combined characteristics of overall SL and thus erratic contributions from individual layers can be avoided. The width $\Delta q_x$ shows periodic oscillations as a function of azimuthal angle $\phi$; hence in-plane RSM presents a strong anisotropy in the diffuse scattering signal (Figure 3.11(a)). Once obtaining the experimental data, the simulations were performed using the model explained in Section 2.2.1. The results shown in Figure 3.11(b) are in excellent agreement with the experimental findings and clearly demonstrate the presence of anisotropically shaped
QDs, elongated along [110] orientation.

Anisotropically shaped SK grown QDs have been reported to show optical anisotropy as observed in their PL emission [112, 115]. In order to study the effect of the asymmetric shape of these ultra-small QDs, we investigated the linear polarization of the PL at 8 K. The sample was excited using right handed circularly polarized non-resonant laser, while a linear polarizer was placed in front of the collecting fiber to analyze the linear polarization of the PL.

Figure 3.12 (a) shows a schematic diagram of the multilayered structure with embedded submonolayer QDs as revealed by the HRXRD analysis. The contour map showing PL spectra as a function of the angle between axis of the linear polarizer and [110] axis of the sample is shown in Figure 3.12 (b).

It was observed that PL emission exhibits strong linear polarization along [110] axis and the corresponding degree of linear polarization (DLP) can be calculated using:

\[ DLP = \frac{I_{[110]} - I_{[1-10]}}{I_{[110]} + I_{[1-10]}} \]  

(3.3)

Where, \( I_{[110]} \) and \( I_{[1-10]} \) are the intensities of the linearly polarized PL emission along [110] and [1-10] orientations respectively. The DLP along [110] axis was found out to

Figure 3.11: (a) Experimental in-plane reciprocal space map around satellite SL(1-1) of (004) Bragg peak depicting clear anisotropic shape. (b) Simulated \( \omega - \phi \) scans verifying the presence of QDs elongated [110] crystal axis.
Figure 3.12: (a) Schematic diagram of the disc-shaped embedded QDs elongated along [110] orientation. (b) Linearly polarized PL spectra plotted as a function of azimuthal angle revealing in-plane anisotropy.

be 0.20. Moreover, the axis of linear polarization and the asymmetric shape of the \( \omega - \phi \) scan show excellent correlation (Figure 3.12) again confirming the presence of elongated QDs preferentially orientated along [110] axis. Thus, this comprehensive technique significantly enhances the ability of extracting structural parameters of embedded ultra-small structures.

### 3.2 Growth and Characterization of Initial Set of Type-II Quantum Dot Solar Cell Samples

Initially, three multilayered structures containing submonolayer ZnTe/ZnCdSe QDs were grown by varying Te fluxes following the procedure discussed in Sections 2.1 and 3.1. The RHEED exhibited a streaky \((2 \times 1)\) reconstruction pattern during the growth of the ZnCdSe buffer layer and the SL. The schematic diagram of the structure along with the MEE shutter sequence is shown in the Figure 3.13 (a) and (b) respectively and the Te source temperatures as well as fluxes are listed in Table 3.2.

The type-II nature of this QD structure was investigated by means of low temperature PL. Figure 3.13 (c) and inset of Figure 3.13 (c) show the PL spectra for all the
three samples for maximum excitation intensity and four orders of magnitude of lower excitation intensity, respectively at 10 K. Figure 3.13 (d) shows the dependence of the PL peak positions on excitation intensity with the peak positions showing strong blue shifts with increasing excitation intensity for all three samples, a typical signature of type-II nanostructures as discussed in Section 2.3.1. The PL spectra of Figure 3.13 (c) also show that there is a significant red shift in the PL peak position in case of samples C52 and C53 with higher Te concentration compared to C51. This red shift in PL emission energy with increasing Te concentration can be attributed to the in-
crease in size, specifically thickness (see Section 3.1), of QDs with the increase in Te source temperature. Since holes are localized in the ZnTe QDs and electrons are free to move in the ZnCdSe barriers, the change in PL emission energy mostly depends on the confinement energy of holes and is fundamentally related to the size of the QDs, which in turn is a function of the Te flux used during the MEE cycles. Thus the hole confinement energy and consequently position of the IB can be controlled by controlling the Te source temperature.

HRXRD analysis was performed in order to extract relevant structural parameters and to calculate associated band gaps and band offsets of the ZnTe/ZnCdSe multilayer type-II QDs. The sharpness and intensities of the visible SL peaks up to forth order for all the three samples as shown in Figure 3.14 (a-c) are indicative of high crystalline quality of the samples. Other than the SL peaks, two additional peaks corresponding to the InGaAs and the ZnCdSe buffer layers were observed very close to the substrate peak as shown in inset of Figure 3.14 (a-c). The in-plane lattice mismatches of the ZnCdSe buffer layers were calculated to be about 0.1% for all the samples indicating that the ternary alloys were almost lattice-matched to the InP substrate. The growth of lattice matched ZnCdSe barriers is important especially to avoid the formation of misfit dislocations, thereby eliminating the possibility of deleterious effects during the device operation. The compositions of the buffer layers, which are nominally same as that of the barrier layers, (shown in Table 3.3) were calculated using the Braggs law (Equation 2.3), assuming that these layers were completely relaxed.

The room temperature band gaps of the ZnCdSe buffer layers, corresponding to

<table>
<thead>
<tr>
<th>Sample</th>
<th>Te Source Temperature in °C</th>
<th>Te flux in ×10⁻⁷ torr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C51</td>
<td>236</td>
<td>0.38</td>
</tr>
<tr>
<td>C52</td>
<td>241</td>
<td>0.63</td>
</tr>
<tr>
<td>C53</td>
<td>250</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table 3.2: Specifications of the investigated samples.
Figure 3.14: (a), (b) and (c) $\omega - 2\theta$ curves for samples C51, C52, and C53 respectively along (004) reflection. Inset: HRXRD peaks corresponding to the substrate and two buffer layers along (004) reflection for each of the sample. (d) $\omega - 2\theta$ curves for the three samples taken along (224) reflection, showing the Braggs peaks corresponding to the substrate, the buffer layers and the first order SL.

The calculated in-plane lattice mismatches of the SL structures for C52 and C53 were found out to be relatively small, about 0.27% for both. The in-plane lattice mismatch for C51 could not be calculated due to very weak SL peak along (224) reflection (Figure 3.14 (d)). The values of the mismatch suggested that the ZnCdSe barrier layers were mostly relaxed and might contain diffused Te, in addition to ZnTe QDs, causing the average SL lattice parameter to increase accordingly in the in-plane
Table 3.3: Summary of the important parameters calculated using HRXRD and absorption measurements along with those obtained from the simulations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Barrier Composition</th>
<th>Band Edge (in eV)</th>
<th>Period (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Simulated</td>
<td></td>
</tr>
<tr>
<td>C51</td>
<td>Zn$<em>{0.49}$Cd$</em>{0.51}$Se</td>
<td>Zn$<em>{0.49}$Cd$</em>{0.51}$Se$<em>{0.99}$Te$</em>{0.01}$</td>
<td>2.09</td>
</tr>
<tr>
<td>C52</td>
<td>Zn$<em>{0.49}$Cd$</em>{0.51}$Se$<em>{0.98}$Te$</em>{0.02}$</td>
<td>Zn$<em>{0.49}$Cd$</em>{0.51}$Se$<em>{0.98}$Te$</em>{0.02}$</td>
<td>2.06</td>
</tr>
<tr>
<td>C52</td>
<td>Zn$<em>{0.50}$Cd$</em>{0.50}$Se$<em>{0.97}$Te$</em>{0.03}$</td>
<td>Zn$<em>{0.50}$Cd$</em>{0.50}$Se$<em>{0.97}$Te$</em>{0.03}$</td>
<td>2.06</td>
</tr>
</tbody>
</table>

direction. Although the Zn$_x$Cd$_{1-x}$Se barriers were almost matched to InP substrate as found from the previous calculations, the vertical lattice mismatch of the SL was found to be about -1.2% (here, negative sign is indicative of tensile mismatch) for all the samples, indicating the presence of a thin layer within the SL with a relatively large tensile mismatch with InP. The origin and nature of this interfacial layer will further be discussed in Section 3.3.

Furthermore, HRXRD based RSM of C51 shown in Figure 3.15 provided preliminary structural information of QD positions. The diffuse scattered intensity was found to be elongated along the $q_x$ direction, indicating the vertical correlation of the QDs within the multilayer structure. The detailed analysis of vertically oriented QDs will be discussed in Section 3.4,
Absorption measurements were carried out on these samples in order to investigate the below band gap absorption occurring due to the possible IB formation within the multilayer QD structure. The below band gap absorption was found to be enhanced due to the presence of ZnTe QDs leading to the observation of small peaks as indicated by arrows in the absorption spectra shown in Figure 3.16. The energy of the below band gap absorption peaks nominally corresponds to the PL peaks of the spatially indirect excitons in this type-II material system (Figure 3.13 (c)). The fact that the below band gap peaks were observed in the absorption spectra in spite of their spatially indirect nature points towards the formation of an IB made out of the hole energy levels, as indicated by the RSM studies. Due to relatively thin submonolayer ZnTe QDs, the hole confinement energy lies close to the ZnCdSe VB as indicated by the position of absorption peaks in Figure 3.16.

Figure 3.16: The plot of normalized absorption for the three samples measured at 10 K. Arrows indicate enhanced below band gap absorption due to presence of ZnTe QDs. Inset: the plot of $(\alpha h\nu)^2$ vs photon energy at room temperature, the data points are fitted with a straight line to obtain the band edges.

The band edges were found to change with the change in Te flux. This observation (the change in band edge with Te flux) was also supported by the presence of near band edge excitonic signature in the absorption spectra of C51, which was missing in C52 and C53 due to increase in relative disorder in addition to increased QD
absorption. The Te fractions in the barriers were then determined using previously calculated ZnCdSe buffer layer compositions and the absorption band edges of the corresponding barriers. Subsequently, the compositions of the Te diffused barriers (Table 3.3) and the corresponding in-plane lattice mismatches with InP substrate were calculated using parameters listed in Table D.2 in Appendix. The lattice mismatches of the barrier with the inclusion of Te diffusion were found to be 0.13% for C51 and 0.29% for C52 and C53, respectively. These values are in good agreement with the in-plane lattice mismatches of the SL calculated from HRXRD data. Moreover, HRXRD simulation results shown in Figure 3.14 (a-c) were found to be in excellent agreement with the parameters calculated by means of HRXRD and absorption measurements (Table 3.3). Most importantly, the simulations confirmed that the barriers are almost lattice matched to the substrate and the tensile mismatch obtained in the HRXRD is solely due to the presence of 0.3 to 0.4 nm (∼1 monolayer) thick strained ZnSe-rich layer at the barrier-QD interface [45].

3.3 Optimization of Growth

In spite of obtaining high quality periodic SL satellite peaks in the HRXRD plot, a relatively high, tensile lattice mismatch was observed between the 0th order SL peak (SL(0)) and the substrate peak as discussed in the previous section. The high tensile mismatch seen in the HRXRD was unexpected as the ZnCdSe spacers were almost lattice matched to the InP substrate, and any mismatch introduced by the presence of the QDs is expected to be compressive, since ZnTe is compressively mismatched to InP with a mismatch of about 3.7% (Figure 3.18). Although, the simulation suggested the presence of an unintentional pseudomorphic ZnSe-rich interfacial layer (IL), about a monolayer thick, forming at the QD-spacer interface, the actual growth mechanism of this layer was unknown.

This IL was thought to be originating from any one of the several possible steps: (i) the Se terminated surface after the growth of the ZnCdSe spacer, which might be forming ZnSe upon Zn exposure during MEE, (ii) the background Se pressure, as the sample was grown in Se-rich conditions, and (iii) the desorption of Cd from
the ZnCdSe spacer during MEE, due to low or no Se flux. While this IL did not adversely affect the optical properties of the structure, the large lattice mismatch of the SL may introduce undesirable degradation effects during future device operation. Thus, in order to examine and improve the growth mechanism of these QD SLs, three samples, C60, C68, and C69 were grown implementing various shutter sequences (Figure 3.17).

Figure 3.17: MEE shutter sequence used during the growth of (a) sample C60 and (b) sample C68.

Samples C60 and C68 were grown by the modified shutter sequences illustrated in Figure 3.17. During the growth of sample C60, the Zn and Cd shutters were kept open for 5 s after the growth of the ZnCdSe spacer to terminate the surface with group II elements instead of Se. This was intended to avoid the formation of ZnSe after Zn exposure in the first cycle of MEE. Also, the Cd shutter was opened along with the Zn shutter during MEE so that if there is any Se present at any time, a ZnCdSe layer would form rather than a ZnSe layer.

A clear change in the RHEED pattern from (2 × 1) to C'(2 × 2) was indeed observed prior to the formation of QDs and during MEE, indicating the complete surface coverage by group II elements (Figure 3.19). Although the surface was terminated...
with the group II elements, the presence of ZnSe-rich strained layer at the QD-spacer interface was again confirmed by HRXRD as shown in Figure 3.19 (a). The mismatch between SL(0) and the substrate peak was found to be almost the same as that of the C51 (Figure 3.20). This result eliminated the possibilities related to the surface termination by Se and to the excess Se pressure, while it pointed toward Cd desorption being the main reason behind the formation of the IL.

C68 was then grown without opening Te shutter during MEE, hence shortening MEE cycles, to confirm that the process of the formation of the strained ZnSe IL is independent of that of the ZnTe QDs formation, and to corroborate the role of Cd desorption in the growth. For C68, the lattice mismatched SL peak along with the periodic satellite peaks was observed in HRXRD plot Figure 3.19 (b), indicating the presence of unintentional ZnSe/ZnCdSe SL. The fact that the lattice mismatch between SL(0) and the substrate peak is lower than that of C51 and C60 suggests that the mismatch is proportional to the duration of the MEE cycles. This result also supports the likelihood of Cd desorption as the cause for formation of the ZnSe-rich IL. Additionally, it is known [116] that the incorporation rate of Cd is lower than that of Zn, and approaches zero at very low Se fluxes. As a result of the difference in
the incorporation rates of these elements, Zn replaces Cd during the growth and gets preferentially incorporated when grown under low or no Se conditions. Moreover, the previous reports [62, 116] support the observation of increased Cd desorption rates at low Se fluxes. This led us to deduce that the Cd desorption together with the preferential incorporation of Zn is leading to the formation of an unintentional strained ZnSe-rich IL at the QD-spacer interface.

Based on the observations from samples C60 and C68, it was concluded that the formation of ZnSe-rich IL cannot be easily avoided during the MEE process. Hence, in order to grow a high quality lattice matched SL with more periods, the approach of strain balancing was chosen. To achieve this, sample C69 was then grown with the same shutter sequence as that of the C68, but with the smaller wait time (3 s) between opening of Zn, Cd, and Te shutters to minimize the desorption of Cd during MEE. Most importantly, intentionally Cd-rich spacer layers were grown in order to compensate the strain introduced by the unintentional ZnSe-rich IL. By carefully adjusting the Cd content in Zn$_x$Cd$_{1-x}$Se, a high quality nearly lattice matched SL was obtained, as confirmed by the HRXRD Figure 3.21 (a). The intentionally lattice
mismatched pseudomorphic Zn$_x$Cd$_{1-x}$Se buffer with the same composition as that of the spacer was grown prior to the growth of the SL in order to measure the spacer composition required for the lattice matched SL and its band gap. In spite of being lattice mismatched, the buffer layer was observed to be of high crystalline quality as indicated by the observation of RHEED oscillations during the growth and the thickness fringes in the HRXRD plot, shown in Figure 3.21 (a). The lattice mismatch in the growth direction of the buffer layer with InP was found to be $\sim 1.35\%$, and the thickness was calculated to be about 90 nm from the thickness fringes and the RHEED oscillations. Using this information and assuming a linear dependence of the lattice parameter (Vegard’s law), the buffer layer composition was estimated to be Zn$_{0.41}$Cd$_{0.59}$Se. Furthermore, the room temperature band gap corresponding to this buffer layer composition was evaluated to be 2.01 eV, using the known the parameters listed in Table D.1 in Appendix. This host band gap is expected to increase by about 18 meV due to compressive strain in the system, calculated using parameters listed in
Table D.2 for this particular ternary alloy composition (for details of the calculations, see Appendix C). Thus, introduction of a Cd-rich spacer in the SL lowered the spacer band gap and brought it even closer to that of the ideal IB-SC host, besides assisting in the growth of lattice matched SL. This result also illustrates an added advantage of this material system, which is the ability to carefully engineer the IB-SC materials by strain balancing to achieve the ideal band structure and the material properties.

The excitation intensity dependent PL at 10 K showed a shift in PL energy Figure 3.21 (b) similar to samples discussed in previous section, demonstrating the type-II nature of the multilayered structure. The PL also showed phonon replicas, separated by the Zn$_{0.41}$Cd$_{0.59}$Se LO phonon energy ($\sim$ 28.3 meV), indicating small amounts of Te diffusion into the spacers and high crystalline quality of the QD SL. Hence, we were able to retain desirable optical properties of this material system, while improving the crystalline quality of the SL by strain balancing technique [117].

3.4 Enhanced Quantum Dot Vertical Correlation

Two samples with the same shutter sequence as C69 were grown by varying Te flux (Table 3.4) during MEE cycles to investigate structural properties of the submonolayer Zn(Cd)Te QDs. $\omega - 2\theta$ scans (Figure 3.22) confirmed high crystalline quality of the samples.

The $\omega - 2\theta$ curves were then simulated to extract the structural parameters using the procedure described in Section 2.2.1 and the important parameters are listed in Table 3.4. It is important to mention that the broader satellite SL peaks in $\omega - 2\theta$ curves are caused by intentional strain balancing same as that of C69, while the surface roughness due to presence of QDs contributes to faster dampening of the peak intensities as compared to the simulated curves for the ideal structure.

Excitation intensity dependent low temperature PL and TRPL experiments were performed in order to check the type-II nature of these structures and to estimate some key material parameters such as QD thicknesses and exciton lifetimes. Both PL and TRPL showed expected behavior with change in excitation intensity (Figure 3.23) confirming the presence of type-II band alignment.
In order to probe into vertical orientation of the submonolayer QDs, HRXRD based reciprocal space mapping was performed. RSM along (002) (Figure 3.24 (a-d)) showed a clear elongation in $q_x$ direction for sample with higher Te fraction indicating enhanced vertical alignment of larger submonolayer QDs in case of C74. Furthermore, to confirm the findings, RSMs were taken along (004) reflection (Figure 3.24 (e-f)). This was done to eliminate the possibility of the broadening related to stain fields surrounding QDs, which inherently depends on the reciprocal lattice vector $q$, while the elongation (i.e. $q_x/q_z$) due to vertical alignment of the QDs is independent of $q$. Similar elongation was indeed observed for C74 RSM along (004) reflection to that of along (002) reflection, confirming the source of elongation to be vertically correlated QDs.

Furthermore, for detailed analysis, the theoretical model explained in Section 2.2.1 was used and thus HWHM along $q_z$ was plotted for SL(-1) for both the samples along both (002) and (004) orientations. An excellent agreement was obtained between the experimental data and the theoretical model confirming validity of the model as well as the presence of diffuse scattering from the QD-like centers. The experimental data shown in Figure 3.25 was then fitted using Equation 2.9 in order to extract the value of $\sigma$ which came out to be about 16.3 Å and 10.5 Å for C70 and C74.
Figure 3.23: PL plots at 10 K for (a) C70, and (b) C74. Inset: The plot of PL peak positions at various excitation intensities; the dashed line represents the fitted curve with cube root of excitation intensity. Behavior of decay time at various excitation intensities for (c) C70 at the detection energy of 2.066 eV, and (d) C74 at the detection energy of 1.937 eV.

respectively. Lateral deviation from one dot to the next can be calculated by means of Equation 2.10, only if the QD diameter is known, which is not available in case of submonolayer Zn(Cd)Te QDs. Hence, supposing the QD size to be about 10 - 20 nm based on the magneto-optical studies [55, 96, 118] performed on the similar material systems (as discussed in Section 2.3.1), the average lateral deviation from one dot to another was estimated to be about 13 - 25% for C70 while 8 - 16% for C74. Therefore, it can be concluded that the average vertical QD correlation increased with the increase in QD size.
Figure 3.24: RSMs along (002) reflection showing substrate, SL(0) and first order SL peaks for (a) C70, and (b) C74. RSMs along (002) reflection showing first and second order satellite SL peaks for (c) C70, and (d) C74. RSMs along (004) reflection showing first and second order satellite SL peaks for (e) C70, and (f) C74.

The enhancement in the vertical QD alignment obtained in case of C74 is supposed to give rise to the uniformity in QD size, improving the structural quality and consequently overall IB-SC performance [79]. Additionally, as discussed in Section 1.1, it is essential to have vertically aligned QDs separated with a thin spacer layer in order to form a miniband within the host semiconductor, which is a fundamental requirement for an IB-SC. To explore the possibility of miniband formation due to enhanced vertical QD correlation in case of C74, detailed comparison of the low temperature PL and TRPL results (Figure 3.26) was done between the samples under investigation.
Firstly, PL line width reduced to $\sim 172$ meV for C74 in comparison to $\sim 197$ meV for C70, indicating less QD size distribution. The widths were measured at very low excitation intensities to nullify the effect of band edge excitonic peak related to the spacer. Symmetric and narrower PL spectrum of C74 supports the result of enhanced vertical alignment as it is supposed to results in well-arranged QDs leading to less size distribution. Secondly, the PL yield obtained in case of C74 was at least 18% more than that of C70 at same excitation intensity (Figure 3.26 (a)) indicating partial suppression of non-radiative recombinations and directing towards the probable formation of a miniband.

To extract characteristic radiative lifetime from the TRPL data, the decay curves were fitted with double exponential decay. Since the carrier concentration is higher and consequently the electron-hole wavefunction overlap is stronger just after the excitation, a rapid decay is observed initially, while at longer observation times the band bending effects become negligible and hence the actual radiative lifetime can be obtained from the second exponential decay. Moreover, in type-II nanostructures the characteristic lifetime is dependent on the QD size and therefore on the detection energy, as a result of the variation in electron-hole wavefunction overlaps. Thus, radiative lifetimes were calculated for both the samples from the fitted decay curves.

Figure 3.25: Plots showing HWHM along $q_z$ for SL(-1) along both the orientations for (a) C70, and (b) C74. The dotted lines are the fit to the experimental data using Equation 2.9. Inset: The intensity profiles along $q_z$ for two selected values of $q_x$. 
Figure 3.26: (a) PL spectra normalized to PL peak of C74 and characteristic radiative lifetime of samples C70 and C74. (b) Experimental and fitted decay curves at various detection energies. Calculated, using TMM, energy levels of holes, confined within the 0.4 nm thick Zn(Cd)Te coupled QDs separated by (c) 2.7 nm, and (d) 4.7 nm thick ZnCdSe spacer. Black solid lines show potential profile whereas red and blue curves are the hole probability densities for each of the two energy levels.

At various detection energies and are shown in (Figure 3.26 (a)). In spite of having larger QDs on an average in case of C74, it was observed that the lifetimes are much lower than those of C70. This can be a result of the overlap between wavefunctions of holes situated in different dots due to enhanced vertical QD correlation in C74, showing again the hints of miniband formation.

In order to verify the possibility of miniband formation as suggested by PL and TRPL results, transfer matrix method (TMM) was employed (refer Appendix Section B.2) inputting the required material parameters listed in Table D.2 in the Appendix. The TMM results shown in Figure 3.26 (c) and (d) demonstrate that the for-
formation of miniband is highly probable in a system of completely correlated Zn(Cd)Te QDs separated by 2.7 nm ZnCdSe spacer in comparison with those separated by larger (4.7 nm) spacer. Therefore RSM, PL, and TRPL data along with TMM calculations confirm overlap of the hole wave functions due to vertical correlation, indicating formation of a miniband, an essential requirement for an IB-SC [91].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sample C70</th>
<th>Sample C74</th>
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<tr>
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<td>250</td>
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<tr>
<td>Te Flux in ×10⁻⁷ torr</td>
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<td>1.2</td>
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<tr>
<td>SL Period in nm</td>
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<tr>
<td>Spacer Composition</td>
<td>Zn₀.₄₈Cd₀.₅₂Se₀.₉₉Te₀.₀₁</td>
<td>Zn₀.₄₆Cd₀.₅₄Se₀.₉₈Te₀.₀₂</td>
</tr>
<tr>
<td>Spacer Thickness in nm</td>
<td>2.25</td>
<td>2.25</td>
</tr>
<tr>
<td>IL Composition</td>
<td>Zn₀.₉₈Cd₀.₀₂Se₀.₉₀Te₀.₁₀</td>
<td>Zn₀.₉₈Cd₀.₀₂Se₀.₈₅Te₀.₁₅</td>
</tr>
<tr>
<td>IL Thickness in nm</td>
<td>0.35</td>
<td>0.37</td>
</tr>
<tr>
<td>QD Composition</td>
<td>Zn₀.₇₈Cd₀.₂₂Se₀.₄₂Te₀.₅₈</td>
<td>Zn₀.₇₉Cd₀.₂₁Se₀.₃₅Te₀.₆₅</td>
</tr>
<tr>
<td>QD-layer Thickness in nm</td>
<td>0.07</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table 3.4: Various parameters for C70 and C74 obtained from experiments as well as simulations.
3.5 Growth Calibration and Optimization for Solar Cell Structures

In spite of obtaining vertically aligned QD structures with a possibility IB formation, considerable enhancement in the below band gap absorption was not obtained. The absence of IB related absorption was attributed to the lack of carriers in the hole energy levels associated with the QDs. Hence, the approach of doping alternate layers of QDs was attempted as shown in the Figure 3.27 (a). Sample CP75 with alternately doped QDs having similar dimensions and density as that of the sample C74 demonstrated slight improvement in the below band gap absorption (Figure 3.27 (b)). Nonetheless, the absorption spectrum indicated that the QD size, density, and composition needed further improvement. A system with a dot thickness of \( \sim 1 \text{ nm} \) and Cd content of \( \sim 60\% \) as shown in Figure 3.29, was found to be a close-to-ideal structure as obtained from simple one-dimensional quantum well calculations.

Thus, to grow larger QDs with higher densities, samples with four Te MEE cycles were grown. Additionally, the shutter sequence was deliberately modified as shown in Figure 3.28 (a), so as to increase Cd content within the QDs. The increase of Cd concentration within QDs is expected to alter the QD composition reducing the
CB offset significantly without much reduction in the VB offset. This is supposed to result in further enhancement of below band gap absorption due to modification of the electronic structure.

As anticipated, C76 sample grown using the revised shutter sequence showed considerable red shift in the PL peak position as compared to that of C74 (see Figure 3.29 (b)). This was attributed to the increase in QD size reducing the hole confinement.

From PL peak energy, it was estimated that the IB lies at about 0.3 to 0.4 eV from the VB. Although this IB position was not ideal, same conditions were later used to grow the QDs in test IB-SC structures. After obtaining satisfactory QD structure, growth of p- and n-type semiconductor layers was also required to be optimized. ZnCdSe host semiconductor can be readily n-doped using chlorine but obtaining p-doping is still a difficult task. Hence nitrogen-doped ZnSeTe was chosen to be the p-type layer. The schematic band alignments of the proposed p-i-n solar cell structure is shown in Figure 3.29.

After several calibrations, high crystalline quality layers of n-ZnCdSe and p-ZnSeTe were obtained. Calibrations were required to obtain lattice matching condition and sufficient doping concentrations. Specifically, it is difficult to control the com-
position of ZnSeTe layers, which effectively modifies the doping concentration [119]. The lattice matched ZnSeTe layers were obtained while growing under Zn-rich conditions and using VCOR valved source for Se. The opening of the valve was kept at \( \sim 23\% \), to maintain the required BEP ratio as shown in Table 2.1 and nitrogen plasma source was used for p-type doping of this layer.

The carrier concentration and mobilities were measured via Hall effect measurements as discussed in Section 2.4.1. Indium has a work function of about 4.1 eV and is suitable for n-contact, while gold has a work function of about 5.3 eV and is suitable for p-contact. Annealing was also required after the deposition of gold on p-ZnSeTe to obtain perfect ohmic contacts. Several growth calibrations were performed in order to obtain high crystalline quality, lattice matched alloys with required electrical properties. The carrier densities and mobilities obtained for the optimized samples are listed in Table 3.5.

Figure 3.29: Schematic diagram showing band line-up of the optimized p-i-n SC structure, under solar illumination. Here \( a \) denotes the band-to-band absorption in the host semiconductor while \( b \) and \( c \) correspond to the below band gap absorption due to presence of QDs.
Table 3.5: Results obtained from Hall measurement, for optimized ternary alloys, nearly lattice matched to InP substrate

<table>
<thead>
<tr>
<th>Alloy Composition</th>
<th>Majority Carriers</th>
<th>Carrier Density in cm(^{-3})</th>
<th>Carrier Mobility in cm(^2)V(^{-1})s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(<em>{0.49})Cd(</em>{0.51})Se</td>
<td>Electrons</td>
<td>(~2.1 \times 10^{18})</td>
<td>(~220)</td>
</tr>
<tr>
<td>ZnSe(<em>{0.57})Te(</em>{0.43})</td>
<td>Holes</td>
<td>(~1.8 \times 10^{18})</td>
<td>(~50)</td>
</tr>
</tbody>
</table>

Upon optimizing individual layers required for an IB-SC fabrication, several attempts were made to grow an actual device. Figure 3.30 (b) shows one of the partially successful IB-SC structures, which was grown after an extensive initial calibration as described above. In spite of which, the structure was very resistive when tested and did not yield consistent I-V results. Later, it was confirmed using HRXRD and SEM (see Figures 3.30 (a) and (b)) analyses, that there was an abrupt reduction in Cd flux due to a malfunctioning of Cd shutter movement.
Chapter 4

Conclusions and Future Directions

The objective of this study was to demonstrate the feasibility of submonolayer ZnCdTe/ZnCdSe QDs as a close-to-ideal IB-SC material system. The key accomplishments towards achieving this goal are summarized below:

1) ZnTe/ZnSe QDs, investigation of size, density and morphology - Optimal growth conditions were obtained by studying MEE-grown type-II ZnTe-rich submonolayer QDs embedded in ZnSe (Section 3.1.1). This was achieved by employing a variety of characterization techniques such as HRXRD, SIMS, PL, and magneto-PL etc. It was shown that the growth mode is analogous to the VW growth, and hundreds of layers can be grown, each containing embedded QDs formed without the formation of WLs. Due to this advantage, they can be incorporated in practical devices such as IB-SCs. Additionally, the size and the density of the QDs can be preferentially controlled by varying Te flux and a number of Te MEE cycles during the sample growth. Such control of QD dimensions and distribution is necessary for any device application.

2) ZnTe/ZnSe QDs, investigation of in-plane morphology - We have developed a comprehensive technique to investigate morphology of these hard-to-image QDs by performing HRXRD based in-plane RSMs complemented with linear polarization dependent PL measurements (Section 3.1.2). This technique demonstrated that these disc-shaped submonolayer QDs are favorably elongated along [110] axis.

3) ZnTe/ZnCdSe QDs, novel multilayer structure for IB-SCs - The sys-
tem of ZnTe/ZnSe QDs was then modified in such a way that the ideal structural as well as optical parameters required for an efficient IB-SC can be attained (Section 3.2). Novel multilayer structures with type-II ZnTe/ZnCdSe submonolayer QDs grown on InP substrates were investigated via HRXRD, PL and absorption to successfully demonstrate that this system has a potential to be an ideal IB-material. The material system was shown to possess desired attributes such as type-II band alignment with ideal band gaps and band offsets, absence of detrimental WLs, and high crystalline quality lattice matched ZnCdSe spacers. Moreover, a possibility of below band gap absorption was also demonstrated, which is an important prerequisite for IB-SC fabrication.

4) Zn(Cd)Te/ZnCdSe QDs, optimization of growth - Although, high crystalline quality SLs consisting of ZnTe/ZnCdSe QDs were obtained, a relatively high, tensile lattice mismatch was observed between SL(0) and the substrate peak. HRXRD measurements and simulations suggested the presence of an unintentional pseudomorphic ZnSe-rich IL, about a monolayer thick, forming at the QD-spacer interface (Section 3.3). Thus, systematic investigation was performed to understand the origin of this layer. Several samples with varied MEE shutter sequences were grown and the detailed characterization was performed predominantly using RHEED and HRXRD. The analysis showed that the growth of ZnSe-rich IL was a consequence of a preferential incorporation of Zn and an increased desorption of Cd during the MEE sequences due to a presence of low (or no) Se flux. To avoid the possibility of material degradation due to this highly strained layer, an approach of strain balancing was chosen. By carefully adjusting Cd content in Zn$_x$Cd$_{1-x}$Se, a high quality nearly lattice matched SL was obtained. Apart from obtaining lattice matching condition, the increase in Cd content in spacer resulted in a slight reduction of the band gap and brought it even closer to that of the ideal IB-SC host.

5) Enhancement in vertical QD correlation and miniband formation - In order to investigate possibility of miniband formation due to vertical self-ordering of the QDs in the optimized structures, HRXRD based RSMs were recoded along various orientations (Section 3.4). Systematic analysis of the RSMs using the model developed by Kegel et al. [82] demonstrated that the vertical QD correlation tends
to increase with the increase in QD size. This pointed towards the likelihood of the miniband formation in case of the sample with enhanced QD vertical alignment, due to the presence of very thin ZnCdSe barriers. This was later verified by performing PL and TRPL experiments, which showed definite indication of the coupling of hole-hole wavefunctions. Finally, a simulation was performed to confirm the findings, which was found to be in complete agreement with the experimental results. Hence, formation of miniband, an essential requirement for a working IB-SC, was accomplished.

6) Growth of Cd-rich QDs, p-ZnSeTe, and n-ZnCdSe - An optimized QD structure as shown in Figure 3.29 was proposed so as to improve the below band gap absorption. This required further modification in terms of QD composition, dimension and distribution. Thus, a new set samples with thicker and denser QDs containing larger fraction of Cd was grown. Additionally, to obtain half-filled IB, attempts were made to dope alternate layers of QDs (Section 3.5). These all measures indeed resulted in the expected outcomes, mainly a reduction in the hole confinement energy and an enhancement in the below band gap absorption. Moreover, high crystalline quality lattice matched p-ZnSeTe and n-ZnCdSe layers, with sufficiently high carrier concentrations and mobilities were successfully grown. Thus, close-to-optimal conditions including structural, optical and electrical properties, required for an actual IB-SC have been successfully achieved. Upon obtaining these essential constituents of the proposed p-i-n IB-SC, some initial attempts were made to fabricate a device structure. Although, growth of the working device is yet to be realized, knowledge gained during this process will certainly be beneficial for future attempts.

Based on the achievements as well as shortcomings of this project, a few essential improvements can be envisioned. Future improvements can broadly be classified in two categories:

A) Optimization of an IB-SC Structure - A systematic modeling is required to improve the design of the SCs in order to enhance the below band gap absorption. The absorption coefficients related to all the involved transitions need to be computed as a function of QD sizes as well as composition to obtain the ideal configuration. This will provide useful insights towards the perfection of the device. The experimental results obtained thus far suggest that a definite enhancement in the absorption can be
achieved by growing thicker QDs while reducing the QD height-to-diameter ratio as reported in Ref. [120]. The increase in QD density as well as growth of large number of QD-containing layers will also result in the required enhancement as mentioned in Ref. [39]. Submonolayer nature of the QDs may restrict further improvement in QD density and size, therefore other growth techniques such as S-K grown QDs and droplet epitaxy can also be explored. Ideal material parameters of the investigated ZnCdTe/ZnCdSe system may actually outweigh the drawbacks of these methods.

The modelling may also help to develop understanding of carrier dynamics, most importantly carrier diffusion lengths. This knowledge can then be applied to design thicknesses and the doping concentrations of individual layers and assess the effectiveness of additional barriers at the interface of p-i and i-n regions.

The p-i-n IB-SC structures are relatively complex and are much thicker than the investigated samples and thus growing a complete sample without a glitch is a challenge by itself. An optimization in terms of lattice matching and appropriate doping is essential to obtain sufficiently high crystalline quality epilayers as required for the working device. Furthermore, an excellent control over the experimental conditions needs to be achieved and sufficient time needs to be invested to be able to reproduce the same structure over and over.

B) Improvements in the Fabrication Techniques - Device fabrication is as important as the growth of the initial p-i-n structure in order to obtain high SC efficiencies. Obtaining ohmic contacts by depositing materials with appropriate work functions is necessary to reduce the contact resistance. Annealing may also need to be performed to obtain good ohmic contacts with very low resistance.

Also, these structures are grown on InP substrates with a buffer layer of InGaAs, both of which are comparatively narrow band gap semiconductors. This makes them unusable as back contact layers and they have to be discarded in the device fabrication processes. There were two different methods which were considered for this purpose:

i) One can remove the substrate and the buffer layer by using the procedure discussed in Section 2.3.2. But this may induce defects due to strain relaxation even if the structure is slightly mismatched. Additionally, it is difficult to work with a thin film of the sample, once the substrate and the buffer layer are removed. This method
was applied in case of IBSC1 but a sufficiently big piece of the sample could not be recovered due to the cracks introduced during the chemical etching process.

ii) The other way is to etch part of the sample until one reaches the bottom n-type ZnCdSe layer and then deposit the n-contact selectively on this bottom layer, while depositing p-contact on the top layer. This method is not ideal as large portion of the bottom layer remains inoperative in terms of carrier extraction but it avoids the substrate removal procedure. This method was also attempted on IBSC1, in which a solution of bromine and methanol was used to etch the part of the sample. This method also did not deliver consistent results, most probably because of the lack of purely ohmic contacts as well as due to poor material quality.

Both the methods of chemical etching resulted in undesirable sample degradation and are required to be perfected in order to fabricate a high quality SC. Furthermore, some lift-off techniques using thin sacrificial layers such as MgS [121] can be advantageous to avoid these degradation issues.

Systematic investigation of the above mentioned issues will surely lead to the fabrication of ultra-efficient IB-SC, owing to the ideal material parameters of the investigated system.
Appendix

A Geometric Structure Factor

This section briefly discusses the diffraction related selection rules for various crystal structures. For a monoatomic face centered cubic structure shown in Figure A.1 (a), atomic coordinates \((u, v, \text{ and } w)\) are \((000), \left(\frac{1}{2}, \frac{1}{2}, 0\right), \left(\frac{1}{2}, 0, \frac{1}{2}\right), \text{ and } \left(0, \frac{1}{2}, \frac{1}{2}\right)\). Thus, using Equation 2.4 following expressions can be derived,

\[
F_{hkl} = f e^{2\pi i(0)} + f e^{2\pi i\left(\frac{1}{2} + \frac{1}{2}\right)} + f e^{2\pi i\left(\frac{1}{2} + \frac{1}{2}\right)} + f e^{2\pi i\left(\frac{1}{2} + \frac{1}{2}\right)} \quad (A.1)
\]

\[
\Rightarrow F_{hkl} = f \left(1 + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(k+l)}\right) \quad (A.2)
\]

This results in \(F_{hkl} = 4f\) for \(h, k, l\) all even or all odd, and \(F_{hkl} = 0\) for \(h, k, l\) with mixed parity.

Similar procedure can be employed to derive an expression for a zinc-blende structure as shown in Figure A.1 (b). For example, ZnSe has four Zn atoms and four Se atoms per unit cell located at \((000)\) and \(\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)\) as well as at the corresponding face-centering translations. Hence, following expression can be obtained,

\[
F_{hkl} = f_{Zn} + f_{Se} e^{\pi i\left(\frac{1}{2} + \frac{1}{2} + \frac{1}{2}\right)} \quad (A.3)
\]

which implies, \(F_{hkl} = f_{Zn} + f_{Se}\) for \(h + k + l = 4m\); \(F_{hkl} = f_{Zn} - f_{Se}\) for \(h + k + l = 2(m + 1)\); and \(F_{hkl} = f_{Zn} \pm if_{Se}\) for \(h + k + l = \text{Odd}\); where \(m\) is an integer.
Figure A.1: A schematic diagram of (a) a face centered cubic crystal structure, and (b) ZnSe, zinc-blende structure.
Table A.1: Strength of reflection as a function of different orientations for a zinc-blend structure computed using expression A.3.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Strength of reflection</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>medium</td>
</tr>
<tr>
<td>200</td>
<td>weak</td>
</tr>
<tr>
<td>220</td>
<td>strong</td>
</tr>
<tr>
<td>311</td>
<td>medium</td>
</tr>
<tr>
<td>222</td>
<td>weak</td>
</tr>
<tr>
<td>400</td>
<td>strong</td>
</tr>
<tr>
<td>331</td>
<td>medium</td>
</tr>
<tr>
<td>111</td>
<td>medium</td>
</tr>
<tr>
<td>420</td>
<td>weak</td>
</tr>
<tr>
<td>422</td>
<td>strong</td>
</tr>
<tr>
<td>333</td>
<td>medium</td>
</tr>
</tbody>
</table>


B  States of Quantum Confined Charge Carriers

In order to calculate the energy and the wavefunction of the quantum confined states in nanostructures such as quantum wells or QDs, one needs to solve Schrödinger equation (SE). Solution of a time independent one-dimensional (1-D) SE for a finite square well potential can work as a good approximation in most of these cases. Following two sections utilize two different approaches to solve 1-D SE.

![Figure B.1](image)

Figure B.1: (a) A schematic of a typical square well potential for an electron in conduction band, here $a$ is the well width. (b) A schematic diagram of a coupled quantum well (QW) structure.

B.1  Graphical Solution of the Finite Potential Well Problem

Following is a typical approach to solve SE for a single finite potential well.

Applying time independent 1-D SE separately to all the regions shown in Figure B.1 (a),

\[
-\frac{\hbar^2}{2m_1^*} \frac{d^2}{dx^2} \Psi_I(x) = (E - V_0)\Psi(x) \quad \text{(B.1)}
\]

\[
-\frac{\hbar^2}{2m_2^*} \frac{d^2}{dx^2} \Psi_{II}(x) = (E)\Psi_{II}(x) \quad \text{(B.2)}
\]

\[
-\frac{\hbar^2}{2m_3^*} \frac{d^2}{dx^2} \Psi_{III}(x) = (E - V_0)\Psi_{III}(x) \quad \text{(B.3)}
\]

where, $m_1^*$ and $m_2^*$ are the electron effective masses in the matrix and the QW, respectively; $\Psi_I$, $\Psi_{II}$, and $\Psi_{III}$ are the electron wavefunctions in corresponding regions. Considering that the wavefunction should go to zero at $\pm \infty$, the bound state solutions to the SEs in each regions are,

\[
\Psi_I(x) = Be^{k_1 x} \quad \text{(B.4)}
\]
\[ \Psi_{II}(x) = C \sin(k_2 x) + D \cos(k_2 x) \]  \hspace{1cm} (B.5)

\[ \Psi_{III}(x) = F e^{-k_1 x} \]  \hspace{1cm} (B.6)

where, \( k_1 = \sqrt{\frac{2m_1^* (V_0 - E)}{\hbar^2}} \), and \( k_2 = \sqrt{\frac{2m_2^* E}{\hbar^2}} \). The corresponding boundary conditions are,

\[ \Psi_I(-a/2) = \Psi_{II}(-a/2) \]  \hspace{1cm} (B.7)

\[ \Psi_{II}(a/2) = \Psi_{III}(a/2) \]  \hspace{1cm} (B.8)

\[ \frac{1}{m_1^*} \frac{d}{dx} \Psi_I(-a/2) = \frac{1}{m_2^*} \frac{d}{dx} \Psi_{II}(-a/2) \]  \hspace{1cm} (B.9)

\[ \frac{1}{m_2^*} \frac{d}{dx} \Psi_{II}(a/2) = \frac{1}{m_1^*} \frac{d}{dx} \Psi_{III}(a/2) \]  \hspace{1cm} (B.10)

Applying above boundary conditions, transcendental equations can be obtained for both, even and odd states. Thus the symmetric solution for \( B = F \) and \( C = 0 \) is,

\[ \frac{1}{m_1^*} k_1 = k_2 \tan \left( \frac{k_2 a}{2} \right) \]  \hspace{1cm} (B.11)

And the antisymmetric solution for \( B = -F \) and \( D = 0 \) is,

\[ \frac{1}{m_1^*} k_1 = -k_2 \cot \left( \frac{k_2 a}{2} \right) \]  \hspace{1cm} (B.12)

These equations can be plotted to extract corresponding eigenvalues.
Following is the Mathematica code used for calculating energy levels of holes confined in Zn(Cd)Te QWs:

```mathematica
hbar = 1.054571628*10^-34
Me = 9.109382*10^-31
eV = 1.60217646*10^-19
Mhhost = 0.589
MhQW = 0.603
Th = 0.4*10^-9
V = 0.75
QW1 = Plot[Sqrt[2*Mhhost*Me*(V*eV - x)]/hbar, {x, 0, 1.4*10^-19}, PlotRange -> Full]
QW2 = Plot[Sqrt[2*MhQW*Me*x]/hbar*(Mhhost/MhQW)*Tan[Sqrt[2*MhQW*Me*x]/(2*hbar)*Th], {x, 0, 2*10^-19}]
QW3 = Plot[-(Sqrt[2*MhQW*Me*x]/hbar)*(Mhhost/MhQW)*Cot[Sqrt[2*MhQW*Me*x]/(2*hbar)*Th], {x, 0, 5*10^-19}]
Show[QW1, QW2, QW3]
```
B.2 Transfer Matrix Method

Transfer matrix method [122, 123] (TMM) is a numerical method that can be applied to a wide range of problems related with second-order differential equations such as SE. We have used this method to calculate hole energy level inside the quantum dots as a function of barrier thickness. This problem is similar to that of the symmetric coupled quantum well system as shown in Figure B.1 (b) and the approach is briefly explained below.

Supposing the effective mass approximation to be valid, time independent 1-D SE for a particle with an effective mass, $m^*(x)$, and moving in a layered structure with a potential, $V(x)$, can be expressed as,

\[
\left[ -\frac{\hbar^2}{2} \frac{1}{d^2} m^*(x) \frac{d}{dx} + V(x) \right] \Psi(x) = E \Psi(x)
\]  

(B.13)

Thus, as in Equations B.4, B.7 and B.9, the wavefunction within $j^{th}$ layer and the corresponding boundary conditions can then be written as,

\[
\Psi_j(x) = A_j e^{\rho_j(x)} + B_j e^{\rho_j(x)}
\]  

(B.14)

\[
\Psi_{j-1}(x_{j-1}) = \Psi_j(x_{j-1})
\]  

(B.15)

\[
\frac{1}{m^*_j(x)} \frac{d}{dx} \Psi_{j-1}(x_{j-1}) = \frac{1}{m^*_j(x)} \frac{d}{dx} \Psi_j(x_{j-1})
\]  

(B.16)

where, $A_j$ and $B_j$ are the coefficients, $\rho_j(x)$ is a complex function and $x_{j-1}$ is the point at the boundary between the two layer. The boundary conditions given by Equations B.15 and B.16 can be repeatedly applied to the wavefunctions to obtain the relation between the coefficients of the first ($A_0$, $B_0$) and the last ($A_N$, $B_N$) wavefunctions in terms of a $2 \times 2$ matrix,

\[
\begin{bmatrix}
A_N \\
B_N
\end{bmatrix} =
\begin{bmatrix}
M_{11} & M_{12} \\
M_{21} & M_{22}
\end{bmatrix}
\times
\begin{bmatrix}
A_0 \\
B_0
\end{bmatrix}
\]  

(B.17)

Now, the amplitude of the wavefunctions should go to zero as $x \rightarrow \pm\infty$. This means that the solution to the SE can thus be obtained by imposing additional boundary condition, namely $M_{22}(E) = 0$, where $E$ is the eigenvalue.
Following are the MatLab codes to calculate energies and wavefunctions of holes confined within ZnCdTe QDs:

```matlab
% Transfer Matrix Method Code 1.
% To calculate the coefficients of the wavefunctions in various regions.
% No input is required, just keep the file open.
function [AB, CD, FG, HI, JK] = QDcoefficientsM(mb0, mw0, Energy, VBO, EGb, EGw, Well_width, Barr_width);
    w = Well_width*1e-10;
b1 = Barr_width*1e-10;
V = VBO;
a = w;
b = (w + b1);
c = (b + w);
h_plank = 1.05457e-34;
q = 1.60218e-19;
E = Energy;
% Effective mass as a function of energy
mw = mw0*(1 + (E)/EGw);
mb = mb0*(1 + (E - V)/EGb);
k = sqrt((2*mw*q)/h_plank);
k1 = sqrt((2*mb*q*(V - E))/h_plank);
M1 = [1, 1; k1/mb, -k1/mb];
Minv1 = [0.5, mb/(2*k1);0.5, -mb/(2*k1)];
I1 = Minv1*M1;
M2 = [0, 1;k/mw, 0];
Minv2 = [0, mw/k; 1, 0];
I2 = Minv2*M2;
M3 = [sin(k*a), cos(k*a);(k/mw)*cos(k*a), -(k/mw)*sin(k*a)];
Minv3 = [sin(k*a), (mw/k)*cos(k*a);cos(k*a), -(mw/k)*sin(k*a)];
I3 = Minv3*M3;
M4 = [exp(k1*a), exp(-k1*a);(k1/mb)*exp(k1*a), -(k1/mb)*exp(-k1*a)];
Minv4 = [(1/2)*exp(-k1*a), (mb/(2*k1))*exp(-k1*a);(1/2)*exp(k1*a), -(mb/(2*k1))*exp(k1*a)];
I4 = Minv4*M4;
M5 = [exp(k1*b), exp(-k1*b);(k1/mb)*exp(k1*b), -(k1/mb)*exp(-k1*b)];
Minv5 = [0.5*exp(-k1*b), (mb/(2*k1))*exp(-k1*b);0.5*exp(k1*b), -(mb/(2*k1))*exp(k1*b)];
I5 = Minv5*M5;
M6 = [sin(k*b), cos(k*b);(k/mw)*cos(k*b), -(k/mw)*sin(k*b)];
Minv6 = [sin(k*b), (mw/k)*cos(k*b);cos(k*b), -(mw/k)*sin(k*b)];
I6 = Minv6*M6;
M7 = [sin(k*c), cos(k*c);(k/mw)*cos(k*c), -(k/mw)*sin(k*c)];
Minv7 = [sin(k*c), (mw/k)*cos(k*c);cos(k*c), -(mw/k)*sin(k*c)];
I7 = Minv7*M7;
M8 = [exp(k1*c), exp(-k1*c);(k1/mb)*exp(k1*c), -(k1/mb)*exp(-k1*c)];
Minv8 = [(1/2)*exp(-k1*c), (mb/(2*k1))*exp(-k1*c);(1/2)*exp(k1*c), -(mb/(2*k1))*exp(k1*c)];
I8 = Minv8*M8;
M9 = [0; 1];
AB = Minv1*M2*Minv3*M4*Minv5*M6*Minv7*M8*M9;
CD = Minv3*M4*Minv5*M6*Minv7*M8*M9; % Minv2*M1*AB;
FG = Minv5*M6*Minv7*M8*M9; % Minv4*M3*CD;
HI = Minv7*M8*M9; % Minv6*M5*FG;
JK = M9; % Minv8*M7*HI;
end
```
% Transfer Matrix Method Code 2.
% To calculate the matrix element M22.
% No input is required, just keep the file open.

function M = QDroots1M(mbx, mwx, EGb, EGw, Energy, VBO, Well_width, Barr_width);

w = Well_width*1e-10;
b1 = Barr_width*1e-10;
V = VBO;
a = w;
b = (a + b1);
c = (b + w);
me = 9.10938e-31;
mb0 = me*mbx;
mw0 = me*mwx;

h_plank = 1.05457e-34;
q = 1.60218e-19;

if E == 0;
E = 1e-10;
end

if E == V
E = V - 1e-9;
end

mw = mw0*(1 + (E)/EGw);
mb = mb0*(1 + (E - V)/EGb);

k = sqrt (2*mw*q)/h_plank;
k1 = sqrt (2*mb*q*(V - E))/h_plank;

M1 = [1, 1, kl/mb, -kl/mb];
M2 = [0, 1; k/mw, 0];

M4 = [exp(k1*a), exp(-k1*a), (kl/mb)*exp(k1*a), -(kl/mb)*exp(-k1*a)];
M5 = [exp(k1*b), exp(-k1*b), (kl/mb)*exp(k1*b), -(kl/mb)*exp(-k1*b)];
M6 = [sinh(k*a), cosh(k*a); (k/mw)*cosh(k*a), -(k/mw)*sinh(k*a)];
M7 = [sinh(k*c), cosh(k*c); (k/mw)*cosh(k*c), -(k/mw)*sinh(k*c)];
M8 = [exp(k1*c), exp(-k1*c); (kl/mb)*exp(k1*c), -(kl/mb)*exp(-k1*c)];

M3 = [sinh(k*b), cosh(k*b); (k/mw)*cosh(k*b), -(k/mw)*sinh(k*b)];
M9 = [sinh(k*c), cosh(k*c); (k/mw)*cosh(k*c), -(k/mw)*sinh(k*c)];
M10 = [exp(k1*c), exp(-k1*c); (kl/mb)*exp(k1*c), -(kl/mb)*exp(-k1*c)];

M11 = [sinh(k*c), cosh(k*c); (k/mw)*cosh(k*c), -(k/mw)*sinh(k*c)];
M12 = [exp(k1*c), exp(-k1*c); (kl/mb)*exp(k1*c), -(kl/mb)*exp(-k1*c)];

M13 = [sinh(k*b), cosh(k*b); (k/mw)*cosh(k*b), -(k/mw)*sinh(k*b)];
M14 = [sinh(k*c), cosh(k*c); (k/mw)*cosh(k*c), -(k/mw)*sinh(k*c)];
M15 = [exp(k1*c), exp(-k1*c); (kl/mb)*exp(k1*c), -(kl/mb)*exp(-k1*c)];

M16 = [sinh(k*b), cosh(k*b); (k/mw)*cosh(k*b), -(k/mw)*sinh(k*b)];
M17 = [sinh(k*c), cosh(k*c); (k/mw)*cosh(k*c), -(k/mw)*sinh(k*c)];
M18 = [exp(k1*c), exp(-k1*c); (kl/mb)*exp(k1*c), -(kl/mb)*exp(-k1*c)];

M19 = [sinh(k*b), cosh(k*b); (k/mw)*cosh(k*b), -(k/mw)*sinh(k*b)];
M20 = [sinh(k*c), cosh(k*c); (k/mw)*cosh(k*c), -(k/mw)*sinh(k*c)];
M21 = [exp(k1*c), exp(-k1*c); (kl/mb)*exp(k1*c), -(kl/mb)*exp(-k1*c)];

M22 = [sinh(k*b), cosh(k*b); (k/mw)*cosh(k*b), -(k/mw)*sinh(k*b)];
M23 = [sinh(k*c), cosh(k*c); (k/mw)*cosh(k*c), -(k/mw)*sinh(k*c)];
M24 = [exp(k1*c), exp(-k1*c); (kl/mb)*exp(k1*c), -(kl/mb)*exp(-k1*c)];

AB = Minv1*M2*Minv3*M4*Minv5*M6*Minv7*M8;
M = AB(2,2);
clear;
Well_width = 4;
Barr_width = 27;
EGb = 2.039;
EGw = 1.837;
mb0 = 0.589;
mw0 = 0.603;
VBO = 0.75;
Range = 10000;
limit = 5e-20;
E = 0: VBO/Range: VBO;
for i=1:Range;
    x = E(i);
    A = QDroots1M(mb0, mw0, EGb, EGw, x, VBO, Well_width, Barr_width);
    if abs(A) > limit;
        B(i) = sign(A)*limit;
    else
        B(i) = A;
    end
end
% Transfer Matrix Method Code 4.
% To plot the wavefunctions of the quantum confined states.
% Input all the required parameters below, including the energies obtained from
% the previous code.

clear;
% Effective mass at E = 0
me = 9.10938e-31;
mbx = 0.589;
mwx = 0.603;
mb0 = me*mbx;
mw0 = me*mwx;

% Simulation Constants
h_plank = 1.05457e-34;
q = 1.60218e-19;
Power = 2; % 1 = wavefunction; 2 = moduli square of wavefunction
scale = 0.2; % Was 0.10 Scale the normalized wavefunction

% SQW or Coupled QW Structure
b0 = -100;
Well_width = 4;
Barr_width = 27;
w = Well_width;
b1 = Barr_width;
b2 = 100;

% Bandgap of Well and Barrier Materials
EGb = 2.039;
EGw = 1.837;

% Valence Band Offset
V = 0.75;
Range = 0.01;

% Energy Levels from QDroots2
Energy_Levels = [0.5575, 0.56074]; % 0.4nm-Qd, 2.7nm-barrier, 0.8eV-VBO A3216
Energy_Levels = [0.5591, 0.5592]; % 0.4nm-Qd, 4.7nm-barrier, 0.8eV-VBO A3216

figure;
for i =1:length(Energy_Levels); % Start of main Loop
E = Energy_Levels(i);
[AB, CD, FG, HI, JK] = QDcoefficientsM(mb0, mw0, E, V, EGb, EGw,Well_width, Barr_width);

mw = mw0*(1 + (E)/EGw);
mb = mb0*(1 + (E - V)/EGb);

% Region (1)
j = 0;
for i=b0:Range:j+1;
   kl = sqrt (2*mb*q*(V - E))/h_plank;
   y(j) = ((AB(1,1)*exp(kl*i*1e-10)) ;
   a(j) = i;
end
% Continue with other regions and calculations...
b(j) = V;
end

% Region (2)
j2 = j;
for i=0:Range:w;
    j2 = j2+1;
k = sqrt (2*mw*q*(E))/h_plank;
y(j2) = ((CD(1,1)*sin(k*i*1e-10)) + (CD(2,1)*cos(k*i*1e-10)));
a(j2) = i;
b(j2) = 0;
end

% Region (3)
j3 = j2;
for i=w:Range:w+b1;
    j3 = j3+1;
k1 = sqrt (2*mb*q*(V-E))/h_plank;
y(j3) = ((FG(1,1)*exp(k1*i*1e-10)) + (FG(2,1)*exp(-k1*i*1e-10)));
a(j3) = i;
b(j3) = V;
end

% Region (4)
j4 = j3;
for i=w+b1:Range:2*w+b1;
    j4 = j4+1;
k = sqrt (2*mw*q*(E))/h_plank;
y(j4) = ((HI(1,1)*sin(k*i*1e-10)) + (HI(2,1)*cos(k*i*1e-10)));
a(j4) = i;
b(j4) = 0;
end

% Region (5)
j5 = j4;
for i=2*w+b1:Range:2*w+b1+b2;
    j5 = j5+1;
k1 = sqrt (2*mb*q*(V-E))/h_plank;
y(j5) = ((JK(1,1)*exp(k1*i*1e-10)) + (JK(2,1)*exp(-k1*i*1e-10)));
a(j5) = i;
b(j5) = V;
end
temp = max(y.^Power);
x = 1:j5;
plot(a(x), (scale*(y(x).^Power))./temp) -E, a(x), -b(x)) plot(a(x), (scale*(y(x).^Power))./temp) +E, a(x), b(x)
drawnow;
xlabel('Thickness (Angstrom)')
ylabel('Energy (eV)')
hold on
end % End of Main Loop
hold off
C Dependence of Band Gap on Internal Strain Fields

Semiconductors with zinc-blend structure typically have three degenerate valence bands at gamma point (i.e. at \( k = 0 \) in reciprocal space). Spin-orbit effects result in the energy modification of one of the bands (split-off band), while other two bands still remain degenerate. In case of heteroepitaxy, lattice mismatch between the epilayer and the substrate results in biaxial strain. Shear components of the strain lead to additional splitting, giving rise to non-degenerate heavy-hole (hh) and light-hole (lh) bands. The degree of lattice mismatch in an epilayer leads to the non-hydrostatic strain components as described below [124, 125],

\[
\varepsilon_{xx} = \varepsilon_{yy} = \frac{a_s - a_e}{a_e} \quad (C.1)
\]

\[
\varepsilon_{zz} = -\frac{C_{12}}{C_{11}} \varepsilon_{xx} \quad (C.2)
\]

where, \( \varepsilon_{xx}, \varepsilon_{yy}, \) and \( \varepsilon_{zz} \) are diagonal elements of the strain tensor; \( a_s \) and \( a_e \) are the lattice constants of the substrate and the epilayer; \( C_{11} \) and \( C_{11} \) are the elastic constants for the epilayer (bulk modulus, \( B = (C_{11} + 2C_{12})/3 \)).

To first order approximation, energies of hh \((E_{hh})\) and lh \((E_{lh})\) can be written as,

\[
E_{hh} = E_0 + a \frac{\Delta \Omega}{\Omega} + \frac{1}{2} \delta E \quad (C.3)
\]

\[
E_{lh} = E_0 + a \frac{\Delta \Omega}{\Omega} - \frac{1}{2} \delta E \quad (C.4)
\]

where, \( a \) is linear hydrostatic deformation potential, \( \Delta \Omega/\Omega = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \) is the change in volume, and \( \delta E \) is the strain splitting. Generally, linear hydrostatic deformation potentials for CB minima \((a_{CBM})\) and VB maxima \((a_{VBM})\) are different and thus separate changes in CB \((\Delta E_C = a_{CBM} \Delta \Omega/\Omega)\) and VB \((\Delta E_V = a_{VBM} \Delta \Omega/\Omega)\) due to change in volume need to be included in Equations C.3 and C.4. Also, \( \delta E = b(\varepsilon_{zz} - \varepsilon_{xx}) \), where \( b \) is shear uniaxial deformation potential. Thus,

\[
E_{hh} = E_0 + (\Delta E_C - \Delta E_V) + b(\varepsilon_{zz} - \varepsilon_{xx}) \quad (C.5)
\]

\[
E_{lh} = E_0 + (\Delta E_C - \Delta E_V) - b(\varepsilon_{zz} - \varepsilon_{xx}) \quad (C.6)
\]
Various material parameters have been used for the calculations related to TMM as well as related to the structural and optical analysis. These parameters have been listed in the following tables.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>ZnSe-CdSe</th>
<th>ZnTe-CdTe</th>
<th>ZnSe-ZnTe</th>
<th>CdSe-CdTe</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT band bowing parameter</td>
<td>0.300 [50]</td>
<td>0.460 [126]</td>
<td>1.621 [127]</td>
<td>0.900 [128]</td>
</tr>
<tr>
<td>RT valence band offset</td>
<td>0.135 [52]</td>
<td>~0.005</td>
<td>~0.930 [53]</td>
<td>~0.800 [54]</td>
</tr>
<tr>
<td>Parameters</td>
<td>ZnSe</td>
<td>CdSe</td>
<td>ZnTe</td>
<td>CdTe</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Lattice parameter (nm)</td>
<td>0.5667 [51]</td>
<td>0.6077 [51]</td>
<td>0.6089 [126]</td>
<td>0.6482 [126]</td>
</tr>
<tr>
<td>RT band gap (eV)</td>
<td>2.690 [129]</td>
<td>1.660 [50]</td>
<td>2.280 [130]</td>
<td>1.480 [126]</td>
</tr>
<tr>
<td>LO phonon energy (meV)</td>
<td>31.8 [131]</td>
<td>25.9 [132]</td>
<td>26.1 [133]</td>
<td>21.4 [133]</td>
</tr>
<tr>
<td>$a_{VBM}$ (eV)</td>
<td>1.23 [134]</td>
<td>0.90 [134]</td>
<td>0.99 [134]</td>
<td>0.89 [134]</td>
</tr>
<tr>
<td>$a_{CBM}$ (eV)</td>
<td>-1.20 [134]</td>
<td>-2.00 [134]</td>
<td>-4.61 [134]</td>
<td>-1.20 [134]</td>
</tr>
<tr>
<td>$b$ (eV)</td>
<td>-1.20 [124]</td>
<td>-0.80 [51]</td>
<td>-1.26 [124]</td>
<td>-2.81 [124]</td>
</tr>
<tr>
<td>$C_{12}$ ($\times 10^{10}$ Pa)</td>
<td>4.98 [124]</td>
<td>4.63 [51]</td>
<td>4.07 [124]</td>
<td>3.94 [124]</td>
</tr>
<tr>
<td>Electron effective mass ($m_e$)</td>
<td>0.16 [53, 85]</td>
<td>0.12 [135]</td>
<td>0.13 [53, 85]</td>
<td>0.096 [135]</td>
</tr>
<tr>
<td>Hole effective mass ($m_e$)</td>
<td>0.75 [53, 85]</td>
<td>0.45 [135]</td>
<td>0.60 [53, 85]</td>
<td>0.40 [135]</td>
</tr>
</tbody>
</table>

Table D.2: Various material parameters used for the calculation. Here $a_{VBM}$ and $a_{CBM}$ are linear hydrostatic deformation potentials for valence band maxima and conduction band minima respectively. Also, $b$ is shear uniaxial deformation potential and $C_{11}$, $C_{12}$ are the elastic constants.
Bibliography


formation of vertically coupled quantum dots in Stranski-Krastanow growth.


