Heterojunction Engineering for Next Generation Hybrid II-VI Materials

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HETEROJUNCTION ENGINEERING FOR NEXT GENERATION HYBRID II-VI MATERIALS

by

THOR AXTMANN GARCIA

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

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Thor Axtmann Garcia

This manuscript has been read and accepted for the Graduate Faculty in chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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ABSTRACT

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Advisor: Professor Maria C. Tamargo

Molecular Beam Epitaxy (MBE) is a versatile thin film growth technique with monolayer control of crystallization. The flexibility and precision afforded by the technique allows for unique control of interfaces and electronic structure of the films grown. This facilitates the realization of novel devices and structures within a research environment normally only achieved though complex industrial processes. In the past, the control of each interface in MBE has been explored to great benefit. In this work, we study the control of these interfaces so as to increase the performance of novel devices material systems. This dissertation focuses on two
main areas in which to manipulate interfaces for our benefit: II-VI Intersubband(ISB) devices and II-VI/Bi$_2$Se$_3$ heterostructures.

Intersubband(ISB) devices, such as quantum cascade(QC) lasers and QC detectors operating in the infrared range, were first realized with this technique. ISB devices offer critical advantages over interband devices especially in the infrared and terahertz range. ISB devices present extremely flexible parameter space for design as they are based on thicknesses of quantum wells(QWs) rather than intrinsic properties of the materials. QC lasers II-VI materials support shorter wavelengths in the infrared than do commercially available III-V materials. ZnCdSe/ZnCdMgSe lattice matched to InP allows for QC laser designs to reach up to 2µm due to a conduction band offset of 1.12eV. Also, the relatively high effective mass and the before mentioned conduction band offset make them attractive for QC detectors. Our research demonstrates that with the use of interface control, novel high performance detectors can be achieved within this material system. Additionally, we consider the future of this material system by exploring MgSe/ZnCdSe short period superlattices as a plausible replacement for ZnCdMgSe in these types of devices.
Topological insulators, a new class of materials, have recently attracted a great deal of attention in the scientific community. Among these, Bi$_2$Se$_3$ has a near ideal Dirac cone at the $\Gamma$ point. Here we demonstrate this material in heterostructures with II-VI semiconductors in order to set the foundation for a new material system for both physical and possible device applications. We also investigate using Bi$_2$Se$_3$ as a virtual substrate for II-VI materials.
Acknowledgments:

A crystal flake does not heed to the whims of the wind and pen snow. There is no singular endeavor in the entirety of the human line that has one face. Thus, this work is caused not from my will alone but the efforts and inspiration of many. The other flakes whisper through every letter and every data point until each breath is one consciousness contained in these pages. Some crystals with hopes and genius inspire, others are the wind that guide us, and yet more are the partners that settle with you on the ground of science. So now by necessity of precision I will dawn a few names to the blizzard that created this venture. I know more will demand with their sorrow my lack of their celebrity upon this page; it cannot be helped and should not be helped. I urge you to accept this token, if your genius is imbedded within the leaf, please know and are urged to know my gratefulness.

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Chapter 1: Introduction

1 Introduction

In solid state physics, a heterojunction is the interface that occurs when two different semiconductors come into contact. Heterojunctions are of paramount importance in the exploration of novel materials and the realization and performance of electronic devices. The quality and properties of these interfaces play a crucial role in the structural, electronic and optical properties of materials. Therefore, it is not surprising that researchers have invested a great deal of resources and effort into the study of heterojunctions since they were first realized. In semiconductors heterojunctions can take three different band alignments opening many possibilities for study and band engineering (figure 1.1). Even though the study of heterojunctions has attracted a great deal of interest over the years, there are many unique opportunities for continued work in this field. In particular, since the opportunity to combine different materials is essentially unlimited, new heterojunctions evolve which require detailed investigation and optimization whenever new materials combinations are considered.

Figure 1.1 A heterojunction between two materials with type I, II, III alignment.

1.1 Overview

The study of heterojunctions of II-VI materials offers an exciting opportunity because of the unique nature of the interfaces needed to realize high quality material and devices. II-VI
materials, if realized in high quality, present a significant advantageous contrast in properties to those achieved by III-V and silicon based semiconductors. Notwithstanding the opportunities that II-VI materials pose, there has been relatively little commercial success to date utilizing this material system. Commercial devices from II-VI materials have been confined to solar cells, which do not require high crystallinity materials, and liquid nitrogen cooled infrared photodetectors based on HgCdTe. This limited success to date is not due to fundamental limitations of the material system, and provides an important opportunity for the realization of novel semiconductor devices.

Despite the lack of commercial success there have been significant advancements in the growth of II-VI materials and devices. These stem primarily from the appeal of wide bandgap II-VI materials in visible light optoelectronic devices before the rise of GaN based semiconductors in this field\(^1\). The progress in visible light electric injection devices was hampered by problems with reduced device lifetimes related to p-type doping\(^2,3\). However, optically pumped devices, for which doping is not needed, still present an opportunity, especially since GaN based longer wavelength visible emitters (yellow-green) have exhibited poor performance. Unipolar devices that only require n-type dopants are also attractive. In particular the ZnCdMgSe materials system lattice matched to InP has a conduction band offset as big as 1.12eV\(^4\), which is appealing for intersubband devices. In addition to those optoelectronic devices, II-VI materials may evolve into new applications when combined with other materials. For example, recently ZnTe/GaSb multilayers were reported for applications as Distributed Bragg Reflectors\(^5\).
Furthermore, topological insulators have recently gained great interest in the physics community. Topological insulators\(^6\) are a new class of materials with conducting surface states that are attractive for spintronics\(^7\) and quantum computation\(^8\). Three dimensional topological insulators based on selenium and tellurium offer a unique opportunity for heterostructures with II-VI materials because of their chemical compatibility and similar growth conditions. In particular, \(\text{Bi}_2\text{Se}_3\) is attractive because it has an ideal single Dirac point at the \(\Gamma\) point\(^9\), spin polarization and the largest bulk bandgap of any known 3d topological insulator. Heterostructures of II-VI and topological insulators present a unique opportunity for engineering new physical phenomena and novel devices. Before this scope can be realized, the epitaxial relationship between van der Waals materials and cubic materials needs to be understood.

A related pursuit is that of the use of van der Waals materials, including \(\text{Bi}_2\text{Se}_3\), as virtual substrates for the growth of semiconductors. This is appealing because in the epitaxy of semiconductors one is usually restricted by the available substrate template. What substrates are available will usually limit the commercial success of a device application. Van der Waals materials relax this constraint because this type of bonding allows the film to grow on many different substrates provided the chemical interaction is small. It follows that if one can grow semiconductor device structures on a van der Waals material then the substrate restrictions are relaxed and novel devices can be realized. II-VI materials present an interesting case study for growth on \(\text{Bi}_2\text{Se}_3\) van der Waals layers due to their chemical compatibility and similar MBE growth conditions. The lack of adequate commercially available II-VI substrates has led to the use of III-V substrates, requiring a heterovalent interface that hampers material quality, thus the possibility of using a virtual substrate is appealing. A more thorough investigation and
methodology of the new heterojunctions formed by these novel materials systems is necessary before their applications can be realized. This is the motivation for the work of this thesis.

The investigation of heterojunctions can be split into three basic aspects: design, growth and characterization. The design of heterojunction is achieved by considering the kinetics, thermodynamics and electronic properties of this interface. The growth of materials with well-behaved heterojunctions, control of the interface chemistry, kinetics and thermodynamics of deposition are necessary. Melt growth techniques, where the crystalline organization is typically governed by diffusion processes, are not adequate. Epitaxial methods such as chemical vapor deposition(CDV), metal-organic chemical vapor deposition(MOCVD) and molecular beam epitaxy(MBE) provide the command of the growth parameters. Among these, MBE with ultra-high vacuum and layer by layer deposition process afford the greatest flexibility and precision. After the growth of samples, a series of characterization techniques provide the essential feedback to further optimize the results.

Figure 1.2: Molecular Beam Epitaxy(MBE) system used in dissertation with three chambers and an ultra-high vacuum transfer mechanism.
1.2 Molecular Beam Epitaxy

Molecular Beam Epitaxy (MBE), in the simplest terms, is an evaporation technique for growing thin epitaxial films and structures of metals, semiconductors and insulators\(^{10}\). Molecular or atomic sources are locally heated and evaporated into beams that are then kinetically transported via an ultra-high vacuum (UHV) environment to crystalize on a heated substrate template. This growth technique has many advantages over other methods in its control over the thermodynamics, kinetics and purity of the thin films that are grown. Single monolayer precision of thickness is routinely achieved and forms the basis of MBE’s ability to allow the growth of engineered nanostructures. The non-equilibrium nature of crystal growth in MBE means that both kinetic and thermodynamic processes take place. The ability to separately control thermodynamics and kinetics facilitates the manipulation of interfaces between contrasting materials. The UHV conditions in MBE allow for very high purity materials and the incorporation of dopants in the crystal. The anatomy of an MBE chamber is quite simple yet, due to the UHV environment, accurate temperature and shutter control and \textit{in situ} monitoring, it has proven to yield unmatched results in many facets of solid state crystal growth.

The experimental setup of a MBE chamber, shown in figure 1.3, demonstrates the simplicity of the setup. On one side of the chamber are the molecular or atomic source materials to be combined in the thin film. The flux of the sources is controlled either by adjusting the individual source temperatures or by a valve. Very high purity materials (typically 6N material), in either their solid, liquid or gas phase, are used. In the case of solid and liquid materials an effusion cell, designed to produce a uniform flux, is employed. These effusion cells are kept at an elevated temperature that produces a desired flux to arrive at the substrate. This flux is measured by ion
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gauges that are moved into the same position as the substrate. The fluxes are additionally controlled by shutters that allow or stop the produced flux. The shutters are usually computer controlled and allow for complex layered crystal structures to be grown by opening and closing certain elements and thus, generate heterostructures. The substrate is also heated to control the kinetics of crystallization. To achieve uniformity, the substrate is rotated. Temperatures of both the effusion cells and the substrate are monitored via thermocouples. The MBE chamber itself is kept at a base pressure of ~10^{-10} torr so that the beams do not experience any collisions before they reach the substrate. The chamber is also surrounded by a cryo panel cooled with liquid nitrogen, or another liquid, in order to maintain a low chamber pressure and ensure thermal

Figure 1.3: Anatomy of a molecular beam epitaxy chamber.
isolation of the sources. To maintain pressure from sample to sample, a separate load lock chamber is employed to introduce samples into the reaction chamber.

Because the chamber is in UHV it allows unencumbered access to the sample while growth occurs. The unique environment facilitates the use of powerful in-situ characterization tools. These characterization tools, common in MBE chambers, include reflection high energy electron diffraction (RHEED), mass spectrometry, diffuse reflectance, ellipsometry, x-ray diffraction (XRD) and pyrometry. RHEED gives MBE the unique ability to observe the surface of the film at the growth front. Pyrometry and/or diffuse reflectance is utilized to augment the accuracy of the temperature reading from the thermocouple. Ellipsometry is typically applied to control the diffractive index of optical device structures. Many MBE systems typically also include ex-situ probes attached by UHV transfer mechanisms such as scanning tunneling microscopy (STM), Auger Electron Spectroscopy (AES), x-ray photoelectron spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES). After the feedback mechanisms are in place, the growth of interfaces can begin to be understood.

The vacuum conditions of the chamber give it the ability to control the reaction at the growth front, make certain that the elements do not react before reaching the growth surface and prevent the incorporation of unwanted impurities. The requirements for the molecular beams can be analyzed by examining the mean free path of the atomic beams being used. One can derive the mean free path ($L$) as:

$$L = \frac{1}{\sqrt{2\pi na^2}}$$

(1.1)
where $d$ is the molecular diameter and $n$ is the concentration of molecules in the vacuum. The concentration is related to temperature ($T$) and pressure ($p$) by:

$$n = \frac{p}{k_B T}$$  \hspace{1cm} (1.2)

where $k_B$ is the Boltzmann constant. By analyzing $L$ and considering that the distance between the effusion cells and the substrate is typically about 0.2m, one finds that a maximum beam pressure of $\sim 10^{-2}$ torr is required to keep elements from combining before they reach the surface of the film. This is much higher than the typical beam pressures of less than $\sim 10^{-5}$ torr typically employed\(^{11}\). If more than one source material is in use at a time, it is the sum of the concentrations and the relevant overlap distance. This requirement does not consider any intermolecular interaction that may take place, and therefore may need to be modified for some applications.

The incorporation of residual impurities is more complicated and depends not only on their concentration, but on the reactivity of the species, growth temperature and growth rate. Although low defect densities can be achieved with growth pressures as high as $10^{-8}$ torr with growth rates around $1\mu$/h at $540^\circ C$\(^{10}\), a lower growth pressure is required if the growth rate and substrate temperature are lower. The relationship between the growth pressure and impurity incorporation can be most clearly seen in the growth of two-dimensional electron gasses\(^{12}\).

Once the atoms reach the substrate, several processes become important in the crystallization of the film. The first is the adsorption and desorption of the atoms that reach the substrate. The relationship between these two processes is defined as the sticking coefficient(s):

$$s = \frac{N_{\text{adsorbed}}}{N_{\text{Total}}}$$  \hspace{1cm} (1.3)
where $N_{\text{Total}}$ is the number of atoms that reach the substrate surface and $N_{\text{adsorbed}}$ is the number of atoms that remain at the substrate. The two main processes of adsorption are chemisorption and physisorption. In chemisorption, a chemical reaction takes place between the substrate and impinging atoms and may involve chemical precursors to facilitate the reaction. Substrate features, such as reactivity, surface orientation and growth steps and defects, play a critical role in this process. On the other hand, in physisorption the atoms are only bonded by weak interatomic forces such as van der Waals interactions. In this process, the chemistry of the species can be neglected and substrate temperature is the primary driving force. Experimentally, it is a combination of both these processes that results in crystallization, with physisorbed precursors leading to chemisorbed crystalline phases.

The interplay between physical adsorption and chemical adsorption changes the way the crystal growth takes place or its growth mode. It is generally accepted that the growth mode is split into three categories: Frank-van der Merwe(FM), Volmer-Weber(VW) and Stransky-

![Figure 1.4: Progression of growth in different growth modes of crystallization. (a) Frank-van der Merwe(FM) or layer by layer growth mode. (b) Stransky-Krastanov(SK) or layer plus island growth mode. (c) Volmer-Webber(VM) or island growth mode.](image-url)
Krastanov(SK). In FM growth mode (figure 1.4a), also called layer-by-layer growth, the growing layer is more tightly bound to the substrate than it is to itself. Complete monolayers are formed before the next layer begins to nucleate creating a smooth two-dimensional crystal. In this growth mode steps can form from one monolayer to the other, and the separation between steps determines the roughness of the film. This growth mode is the desired one for superlattices and heterostructure materials where smooth interfaces between layers are required. SK growth, or layer plus island growth, is like FM growth mode, except that after forming an initial wetting layer of one or more monolayers the growth energetics become unfavorable and islands begin to form. This growth mode has been exploited for the growth of quantum dot structures by MBE. In VW, or island growth, the growing film is more tightly bound to itself than the substrate leading to small clusters nucleating on the surface of the film and then growing into islands. This growth mode is typical of van der Waals materials such as Bi$_2$Se$_3$ where there is weak bonding to the substrate. Which mode is present in a film is determined by the properties of the substrate and the growing layer and can be controlled by modifying the interplay between the kinetics and thermodynamics of growth.

In addition to the growth mode, atomic diffusion processes happen at the growth front in MBE and can determine the crystal phase and topology of the crystal. Surface diffusion is the distance traveled by atoms on the surface before they reach a bonding site (figure 1.5). Surface diffusion plays a critical role in the growth mode as well as atomic aggregation in the growth front. Surface diffusion depends on the binding energy, the momentum of the atoms when they reach the growth surface and the interatomic interaction of arriving atoms. The distance and speed of atoms in this process is called the mobility of a species at a given temperature. When growing
alloys, the competition between the mobilities of the different atom constituents plays a significant role in the morphology and optimal growth temperature of the film. Atoms may also interact with the layers underneath the surface in a process called interdiffusion. Interdiffusion depends on the size and mass of surface atoms as well as the binding energy competition between surface layers and subsurface layers. Interdifusion often determines the abruptness of interfaces, or even what crystal phases are realized in the growing film. Experimentally, it is a combination of all these processes that determine how epitaxy proceeds. The interplay between all the possible mechanisms that take place in crystal growth can be understood but are often difficult to predict theoretically and must be determined experimentally.

1.3 Parameters for Epitaxy

We will now explore some of the different parameters that determine the crystal growth of crystals in MBE. These parameters can be divided into several general categories. The first of these is the crystal structure compatibility between the substrate and the growing crystal. The
second is the surface energy of the growth surface. The third is the thermodynamic stability of the crystal.

![Graph showing lattice constant vs. bandgap for II-VI and III-V zinc blende and diamond binary semiconductor alloys. The lattice constant for the InP substrate is shown as a dotted line. Purple lines indicate the bowing parameters of II-VI Selenide in this thesis and green lines that of III-V alloys used.](image)

### Figure 1.6: Lattice constant vs. bandgap for II-VI and III-V zinc blende and diamond binary semiconductor alloys

**1.3.1 Lattice Constant**

The most basic epitaxial relationship is that of the alignment of atoms in epitaxial growth. This alignment can be quantified by examining the spacing between atoms in a crystal or its lattice constant. Binary alloys have well-defined lattice constants for each phase of the crystal. For example, for zinc blende II-VI and III-V binary alloys the lattice constant in the (001) direction is summarized in figure 1.6; as seen here, the lattice constant of InP as the substrate, shown by a dotted line, MgSe is closely lattice matched. The lattice constant can be changed by combining two binary compounds, for example ZnSe and CdSe. The lattice constant resulting from different fractions of each binary can be approximated to good precision with the use of Vegard’s Law:

\[
a_{A(1-x)B_x} = (1 - x)a_A + xa_B
\]

(1.4)
where A and B are the components before mixing and $a_{A(1-x)B_x}$ in the lattice of the solution. In our example of ZnSe and CdSe we need a composition of 0.49 Zn and 0.51 Cd in the Zn$_{x}$Cd$_{(1-x)}$Se alloy to match the lattice constant of InP.

This direct relationship assumes that the two crystals are of the same crystal structure and are growing in the same orientation as illustrated by the two cubic structures in figure 1.6a. However, there are other possibilities for matching the lattice such as those seen in figure 1.6a-c. The first is that of cube on cube relationship where the lattice constant of the growing layer to the substrate can have a ratio of 1 (figure 1.7a) and 1/2 (figure 1.7b). The second relation is 45°-rotated alignment, where the growing layer is rotated 45° to the substrate. Here the lattice constant can take a ratio of $\frac{1}{\sqrt{2}}$ (figure 1.6c) and $\sqrt{2}$ . Other rotations are possible but they decrease the symmetry and are therefore energetically unfavorable and difficult to control experimentally. Additionally, it is important to be aware of the existence of other crystalline orientations.

![Figure 1.7: Possible lattice constant matching options in cubic structures. (a) and (b) show possible cube on cube relationships (c) show 45° rotated alignment.](image-url)
producing polycrystalline material as those phases may occur even if energetically unfavorable. Non-cubic lattice matching is also possible in hexagonal and (111) directed growth of cubic crystals, for example; here the symmetry of the growing layer needs to be considered and may lead to rotation phase domains and twining.

If the lattice constants of the substrate and the growing crystal do not match, there are several processes that can take place to accommodate epitaxy. The first is a distortion in the crystal. For zinc blende crystals, a tetragonal distortion that breaks symmetry can occur to accommodate the mismatch between the layer and the substrate. To maintain the same atomic density for lattice constants that are smaller than the substrate, the lattice elongates in the growth direction and, for lattices that are bigger, the lattice compresses. When a layer grows in this modified form it is called pseudomorphic growth. The symmetry breaking compression and elongation has an associated energy, referred to as strain ($\varepsilon$). This strain energy increases as the crystal grows and can lead to a change in the growth mode, as happens in SK growth; or it can lead to a break in the periodicity of the lattice by the skipping of atoms and subsequently, the relaxation of the crystal to its natural cubic lattice. When relaxation happens this way, the skipping of atoms is known as misfit dislocations, usually with deleterious effects on the quality of the crystal. The thickness of a strained layer that can be grown before relaxation occurs is known as the critical thickness. The critical thickness ($h_c$) can be estimated using the following relation\textsuperscript{18}:

$$h_c \approx \frac{b}{f} \cdot \frac{1}{4\pi(1+v)} \cdot \left( \ln \left( \frac{h_c}{b} \right) + 1 \right)$$  \hspace{1cm} (1.5)$$

where $h_c$ is the critical thickness, $b$ is the magnitude of the Burger’s vector, $v$ is the Poisson ratio and $f$ is the mismatch between the growing layer and the substrate defined as:

$$f_m \approx \frac{a_{\text{layer}} - a_{\text{substrate}}}{a_{\text{substrate}}}$$  \hspace{1cm} (1.6)$$
where \( a \) is the lattice constant of the substrate and layer. When calculating the critical thickness, one finds that it is very small compared to useful material growth. However, in MBE there are several ways of extending the critical thickness such as the use of surfactants to reduce the strain energy at the growth front and by controlling the surface kinetics with substrate temperature or grow rate. Typical pseudomorphic growth in MBE far exceeds the critical thickness that is calculated by equation 1.6.

### 1.3.2 Surface Energy

The parameters that determine the growth mode of the film are summarized by a single parameter known as surface energy, or interface energy\(^\text{13}\). The surface energy is the amount of energy that is required when a new surface is created. Surface energy includes not only the cohesive energy but also surface reconstruction and interface states that may occur during epitaxy. There are three components to an interface in epitaxy of crystals: the substrate(A) (or template), the growing layer(B) and the interface(Int). If the surface energy of the substrate(\( \gamma_A \)) is greater than the sum of that of the interface(\( \gamma_{\text{Int}} \)) and of the growing layer(\( \gamma_B \)), the growth(\( \gamma_A > \gamma_{\text{Int}} + \gamma_B \)) will proceed by FM (layer by layer, figure 1.4a) growth mode. If the inverse is true and the surface energy of the substrate is less than the surface energy of the growing layer (\( \gamma_A + \gamma_{\text{Int}} < \gamma_B + 2\gamma_{\text{Int}} \)), the growth of the layer will proceed in VW growth mode (island growth, figure 1.3c). Obviously, to have sharp interfaces two-dimensional growth is the desired growth mode. When lattice mismatch is present in the system an additional term is added (the strain) and 2d growth proceeds until that term becomes dominant. This mode is called SK growth mode. A quick glance at the situation above would lead one to believe that heterostructures layers of A-B-A-B are not possible. However, one can alter the surface energy by use of surfactants, changing
the reconstruction, altering the growth symmetry, strain and the addition of interfacial layers. Island growth mode can also be suppressed to create pseudo-2d growth by reducing the growth temperature and/or increasing the growth rate\textsuperscript{19}. The growth mode and surface reconstruction can be experimentally verified using reflected high energy electron diffraction (RHEED) during the growth of the crystal.

Unfortunately, surface energy and interface energy are difficult to measure accurately. These experimental limitations look to computer modeling in order to simulate the surface energy of semiconductor surfaces\textsuperscript{20-22}. How to set up these calculations is explained later in the chapter.

1.3.3 \textit{Thermodynamic Stability}

Even if the crystal structure and surface energies are favorable it does not mean that the interface between two compounds is thermodynamically stable. This is particularly true for heterovalent interfaces, or interfaces with a change in valency across the interface, where charge imbalance causes chemical reactions between the growing layer and the substrate. These reactions manifest themselves several ways during crystalization. The first phenomenon is interdiffusion. Interdiffusion causes the interface to lose its abruptness and can lead to unwanted phases in the crystal. Another phenomenon common to thermodynamically unstable interfaces is the formation of other compounds at the interface; these compounds may manifest themselves as staking faults in the film. Predicting thermodynamic behavior requires detailed knowledge of the phase diagrams for the alloys, which is not always available. They can also be predicted by utilizing molecular dynamics (MD) simulations, or by using density functional theory calculations to examine the forces in different interface configurations. For heterovalent interfaces (an interface
with a change in valency) one simple way to determine the electronic stability of an interface without DFT calculations is by using the so-called electron counting method (ECM)\textsuperscript{23}. For the case of III-V alloys, in each bonding orbital group III elements contribute 3/4 electrons and group V elements 5/4. In each II-VI bonding orbital, group II contributes 2/4 electrons and group VI, 6/4 electrons. It follows that a II-V bond is electron deficient, and a III-VI bond is electron rich. The high concentration of electrons in a small volume at the interface is thermodynamically unstable and reactions take place. The polar nature of this imbalance is strong enough to lead to enhanced ionic desorption or diffusion\textsuperscript{24}. The solution to problems arising from thermodynamic instability are often complicated and are usually determined experimentally through crystal growth. MBE is currently the best available method for dealing with thermodynamically unstable interfaces due to its rich control over kinetics.

1.3.4 Symmetry

When dealing with compounds without symmetry in the growth direction or when growing alloys epitaxially with a different crystal structure from that of the substrate, symmetry must be considered. Symmetry problems can be summarized in the following manner: it is easier for a material with a higher symmetry to grow on a material with lower symmetry without the formation of orientation (twin) domain and translational domain boundaries because of the increase in symmetry of the growing material. When the opposite is performed and a material with lower symmetry is grown on a material with higher symmetry, there are symmetry operations that are possible in different parts of the film creating phase domains. In practice, it is very difficult to eliminate an available symmetry operation, but there are several methods available in MBE to suppress them. One method is to reduce the symmetry of the substrate using
vicinal or stepped substrates. Another approach is to use buffer layers to energetically favor one of the symmetry directions over the other; this way is difficult as it requires careful control over the kinetics and thermodynamics of growth. A third method is to grow the film in the highest symmetry direction; for example, GaAs is typically grown in the (001) direction rather than the (111) direction as the (111) direction is less symmetrical. Symmetry problems are of course the most pronounced when growing low symmetry materials such as hexagonal materials. Materials with weak bonding, such as two-dimensional van der Waals materials, have the further complication that symmetry operations energetically like these make finding appropriate buffer layers challenging.

1.4 Theoretical Calculations and Modeling

In the development of the work explored in this dissertation the growth of materials has been educated by a series of structural modeling and electronic structure engineering methods. The methods in this section were used to help design experiments and aid in the design of experiments as well as explain specific observed behavior. Although theoretical treatments are not the main thrust of our efforts, it was necessary to develop a rudimentary understanding of their basis, and basic methodologies for their implementation. In this section, we present an introduction to the fundamental basis of techniques applied and a brief description of some of the calculations that were performed. The following descriptions are not meant to provide a complete understanding of the techniques applied. The techniques in this section are divided in two general directions: structural simulations utilizing density functional theory (DFT) calculations and band structure engineering applying envelope function approximations.
1.4.1 Structural Simulation Utilizing Density Functional Theory (DFT)

Structural modeling deals with the stability of a prepared interface and our ability to grow the materials we intend in MBE. Solid state modeling and simulations is a very rich field so, we confine our scope to only the simplest and most useful DFT modeling needed to grow materials and devices via MBE used here. All simulations, unless otherwise stated, were done with the quantum espresso package for DFT simulations. Pseudo potentials used for structural simulations were generated using inputs from Andrea del Corso’s pslibrary. Ultrasoft pseudo potentials with relativistic corrections were used to account for the influence of core electrons. Nonlocal exchange correlation functional was employed in the Perdew-Burke-Ernzerhof (PBE, PBESol) parametrization. All structures were relaxed before calculations with the notable exception of van der Waals materials where bonding energetics are still an area of active research.

The first parameter to be simulated is that of surface energy. The surface energy of different reconstructed surfaces can be simulated to determine the ideal surface for epitaxy. Computationally, this is difficult as there are many atoms involved in a surface reconstruction. A good estimate can be verified with the use of first principle methods utilizing density functional theory (DFT) to model the surface energy. For example, we can get a good estimate of the relative surface energies for each GaAs reconstructed surface by utilizing a slab geometry in the following formulation:

\[
\gamma = E_{slab}^{total}(N_{Ga}, N_{As}) - (N_{Ga} + N_{Ga})E_{GaAs}^{Bulk} - \Delta N\mu_{As}
\]  

(1.7)

where \( \gamma \) is the surface energy, \( E_{slab}^{total} \) is the total energy calculation of a slab in formula units, \( (N_{Ga} + N_{Ga})E_{GaAs}^{Bulk} \) is the total energy in the slab from its bulk components and \( \Delta N\mu_{As} \) is the
chemical potential of excess As atoms on the surface. A complete derivation of this formula was completed elsewhere\textsuperscript{22}. A diagram of the slab for the GaAs $\beta_2$ (2x4) reconstruction can be seen in figure 1.8. Note that slabs are repeated infinitely in all directions when performing calculations. In order to reduce the influence of repeating slabs on each other, pseudo-hydrogens are used to passivate the bonds on one of the slab surfaces. The contribution of the pseudo-hydrogens to the total energy must be taken into account. It follows from the derivation, that the chemical potential depends on the equilibrium pressure of the arriving elements and temperature of the substrate\textsuperscript{22}. Since this is the case, one can vary the chemical potential in the last term in order to determine the surface energy and stability of different surface phases relative to each other and to the growing film on top.

Figure 1.8: Slab geometry used for density functional theory calculations of surface energy for a given surface reconstruction.
Much simpler DFT cohesive energy calculations can be employed to compare surface energies of different compounds when the reconstruction is the same. The validity of this approach, and a detailed comparison was previously explored by others and has been found to yield a good approximation to experimental results. Cohesive energy calculations were performed by first minimizing the lattice constant of the bulk binary and bulk elements in the material of interest. This is followed by a total energy calculation of the bulk elements and bulk binaries. The total energy values are then subtracted from each other to arrive at the cohesive energy of the binary solid. Thermodynamic stability can also be estimated by looking at the relative cohesive energies of the crystals in a heterojunction and evaluating the temperatures in which they are grown.

As is the case for surface energy one can also simulate the interface itself with DFT in a slab geometry. This is accomplished by taking two relaxed bulk materials, joining them and analyzing the forces that exist at the interface. An even more complete analysis can be achieved utilizing these forces and letting them act on the interface atoms in molecular dynamics (MD) simulations.

### 1.4.2 Band Engineering Calculations for Heterostructure Design

Even though a full solution to the many electron Schrödinger equation is considered the best method for determining the electronic structure of semiconductors, it fails in practice because of the high computational cost. Many approximations have been used successfully to deal with this problem especially when it comes to macroscopic materials such as band engineered superlattices and devices. One such method is the envelope function approximation. This procedure has been very successful for the simulation of electronic devices such as quantum
cascade (QC) lasers and detectors presented here. Single and multiple charge carrier versions of this approximation are incorporated to determine the band structure of the conduction band as well as band to band transitions in semiconductor quantum wells. A single electron envelope function approximation with an effective mass approximation is used to determine the energy levels in quantum wells in intersubband (ISB) materials and devices. When simulating band to band transitions a transfer matrix method is applied to determine the energy of electrons and holes in the structure. For pseudo-infinite structures such as short-period superlattices (SPSL), the Kronig-Penney model is employed. Even though these methods yield approximations, they are widely used; good agreement with experimental results can be achieved by these methods and they can be used to guide structure design.

1.4.2.1 Envelope Function Approximation

In this approach, we assume that electrons in quantum wells behave like free electrons except that the mass of the electron is replaced by an effective mass for each material. This modification considers the periodic potential in a crystal. Charge carriers in a periodic potential are described with the use of a Bloch function:

\[ \Psi(\vec{r}) = u(\vec{r})f(\vec{r}) \]  
(1.8)

where \( u \) is a rapidly varying function reproducing the periodic potential in the crystal lattice and \( f \) varies slowly within the interatomic length scale simulating the energy levels of a quantum well. One must note that the envelope function \( f(\vec{r}) \) is a plane wave, \( e^{i\vec{k}\cdot\vec{r}} \). With this in mind, the Schrödinger equation for the envelope function can be written as:

\[ -\frac{\hbar^2}{2m^*} \nabla^2 f_i(r) + V(r)f_i(r) = E_if_i(r) \]  
(1.9)
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Here \( f_i(r) \) is the wave function, \( m^* \) is the effective mass and \( V(r) \) is the height of the well. To further simplify equation 1.9, we can separate the in-plane and out-of-plane motion to arrive at the one-dimensional Schrödinger equation for one of the bands:

\[
-\frac{\hbar^2}{2m^*} \frac{d^2 \phi_n}{dz^2} + V(r) \phi_n(z) = E_i \phi_n(z) \tag{1.10}
\]

Formula 1.10 can then be used for each layer in the structure, changing the effective mass for each material and applying the proper boundary conditions. The boundary conditions can be defined for wells and barriers as follows:

\[
-\frac{\hbar^2}{2m_b^*} \frac{d^2 \phi_b}{dz^2} + V(r) \phi_b(z) = E_i \phi_b(z), \quad \phi_b = B e^{kz}, \text{for}\quad z \leq -\frac{l_w}{2} \tag{1.11}
\]

\[
-\frac{\hbar^2}{2m_w^*} \frac{d^2 \phi_w}{dz^2} = E_i \phi_w(z), \quad \phi_w = A \cos(kz) - \frac{l_w}{2} \leq z \leq \frac{l_w}{2} \tag{1.12}
\]

\[
-\frac{\hbar^2}{2m_b^*} \frac{d^2 \phi_b}{dz^2} + V(r) \phi_b(z) = E_i \phi_b(z), \quad \phi_b = B e^{kz} \quad z \leq \frac{l_w}{2} \tag{1.13}
\]

where \( m_b^* \) and \( m_w^* \) is the effective mass for wells and barriers and is the \( \phi_b \) and \( \phi_w \) are the wave functions for each. The envelope function approximation makes two basic assumptions: the effective mass is a valid approximation of bulk crystal and a heterojunction between two materials can be described by a difference in bandgaps.

1.4.2.2 Kronig-Penney Model

When the electron wave function is no longer localized in individual wells in a pseudo infinitely repeating structure, such as a short period superlattice, electrons and holes experience a periodic potential that can appear to be infinite as in a bulk crystal. When this occurs, charge carriers have an equal probability of being in any of the individual quantum wells in the system. Due to the
Pauli exclusion principle, electrons in this type of system form mini-bands whose energy can be solved by treating the entire periodic potential of the repeating structure. A good approximation for the position of these mini-bands can be achieved with the Kronig-Penney model for short-period superlattices\(^3\). In this scheme, the definition of the unlocalized wave function can be understood by a periodic potential thus:

\[
\phi(z + L) = e^{i(kz + kL)} = e^{ikz} e^{ikL} \tag{1.14}
\]

where \(L\) is the size of the period of the infinite superlattice. A more complete derivation and implementation of this model can be found elsewhere\(^3\). This model has been shown to give good agreement with experimental results and is extensively used in chapter 5.

1.5 Materials and Device Applications

This section is an introduction to the materials and device applications explored throughout the dissertation: intersubband(ISB) devices, topological insulators and virtual substrates.
Chapter 1: Introduction

1.5.1 Intersubband(ISB) devices

As discussed in the preceding section, quantum confinement in quantum wells gives rise to quantized energy levels in a quantum well. Adjusting these energy levels by modifying quantum well thicknesses and tunneling between wells, allows for the creation of artificial materials with precisely positioned energy levels (figure 1.9). Two types of transitions can be exploited from these precisely controlled energy levels. First, transitions from the valance band to conduction band energy levels, so called band to band transitions. Second, transitions between quantized energy levels in either the conduction band or valence band, so called intersubband(ISB) transitions. ISB transitions have unique advantages over band to band transitions. Since the curvature in k-space of these transitions is the same, they are essentially symmetrical giving rise to sharp transition profiles. Additionally, they exhibit faster relaxation times since transitions can occur without any recombination processes. Another advantage is that ISB transitions are directly tied to quantum well widths and not the electronic properties of the material being used. The last advantage is crucial in infrared and terahertz devices where materials with bandgaps small enough to emit or absorb the infrared are prone to thermal excitation of electrons thus, degrading the performance and necessitating cooling. Although many types of ISB devices are possible, we focus only on those presented in this document.

1.5.2 Quantum Cascade(QC) lasers

In 1971, building upon their work on superlattices, Soviet scientists Kazarivov and Suris theorized that one could achieve amplification of electromagnetic waves with the use of ISB transitions.
This amplification became known as a quantum cascade (QC). In 1994 Jerome Faist, Federico Capasso and colleagues utilized the precision afforded by MBE to realize the first QC laser. The band diagram for this first quantum cascade laser is illustrated in figure 1.10a. The design of such band diagrams is engineered by solving the Schrödinger equation for each quantum well with the envelope function approximation. The moduli squared from the relevant wave functions are shown in the figure; the illustrated forward tilt in the wells is from an applied bias. These band diagrams directly translate into physical layer thicknesses in a thin film. In this

Figure 1.10: (a) Simplified conduction band diagram for quantum cascade (QC) laser. (b) Conduction band profile of a QC laser complete with injector and active region energy levels.
device electrons are injected though an AlInAs barrier into the E₃ energy level of the active core. The overlap between E₃ and E₂ ensures population inversion into an InGaAs well with emission energy equal to the difference between the two excited energy states. The presence of the E₁ energy level reduces the lifetime of electrons in that lower energy state so that they can thermalize quickly into the injector; to accomplish this they must be separated by an LO phonon. The injector region is a graded mini-band that under bias allows the electrons to move to the top of another active region (figure 1.10b). The process is therefore repeated, essentially generating multiple photons for each electron injected into the structure with some loss due to leakage and scattering. The well injector pair is usually repeated 20 to 50 times depending on the material system. The core of the device is usually surrounded by waveguides to form the cavity of the laser so that stimulated emission can take place. Utilizing this scheme, we can generate a laser device from any material system in which quantized energy levels are possible, including the ZnCdSe/ZnCdMgSe devices presented in this dissertation.

Figure 1.11: Simulation of the conduction band of a quantum cascade detector (QCD)
1.5.3 *Quantum Cascade (QC) detectors*

Quantum cascade (QC) detectors or QCDs are similar in design to QC lasers but, instead of a bias being applied, light is absorbed to create a bias in the device. In this kind of device, photons are absorbed by promotion of electrons in intersubband energy levels. Likewise, the active well absorbs a photon equal to the energy difference between the two intersubband energy levels. The promoted electrons then tunnel to decreasing energy levels until they settle on the next active well in the cascade (figure 1.11). This activity has the effect of inducing a bias in the device because there will be more electrons in the wells down the line. As one can see, this is a photovoltaic device where one measures the voltage across the device instead of current changes like in other ISB devices such as quantum well photodetectors. This photovoltaic device is not prone to noise from current sources; its muted noise is at the expense of detectivity. Although the detectivity is lower, the reduced noise means that these devices outperform their counterparts. Additionally, they are very low power and require relatively simple measurement electronics meaning that they can be used as infrared sensors in “internet of things” devices. In this dissertation, we explore novel QCD devices utilizing the ZnCdSe/ZnCdMgSe material system.

1.5.4 *Topological Insulators*

Progress in physics and electronics is often driven by new engineering schema or by the discovery of new materials. Recently the discovery of a new class of materials coined *topological insulators* with unique quantum mechanical properties represent such an event. These materials have insulating bulk, but metallic surface states or edges that are protected from scattering due to their peculiar topology (figure 1.12a). Topological insulators fall into three general categories: 1d, 2d and 3d. 1d topological insulators occur in a quantum wire where the
ends are conducting; 2d in a quantum well where the edges are conducting; and 3d in bulk materials where the surfaces are conducting. Here we focus on 3d topological insulators and specifically Bi$_2$Se$_3$. Among 3d topological insulators, Bi$_2$Se$_3$ is probably the best studied due to its nearly ideal single Dirac cone at the Γ point in the Brillouin zone and relatively large bandgap (~0.3eV). Figure 1.12a illustrates the insulating bulk conduction band and valence band with the conducting surface states of a 3d topological insulator as well as where the current direction is locked with momentum and spin-making backscattering improbable. When looking at energy momentum space, the surface states have a helical motion around the Dirac cone (figure 1.12b) that is like that of graphene. In this dissertation, we explore the combination of Bi$_2$Se$_3$ with II-VI semiconductors as a new hybrid material system or heterostructure; we do this not only to explore the topological properties of Bi$_2$Se$_3$ but to modify and take advantage of them in devices. This is a first step in moving towards engineered materials that contain topological insulators as building blocks.
1.6 Characterization

To determine the properties of the grown crystal many characterization techniques were employed in the realization of this thesis. In this section, we give an introduction to those techniques that are used the most often used throughout our work. These methods include diffraction techniques including reflected high energy electron diffraction (RHEED), x-ray diffraction (XRD), and x-ray reflectance (XRR). Optical probes were also used including photoluminescence spectroscopy (PL), contactless electro-reflectance (CER) and Fortier transform infrared spectroscopy (FTIR). Hall effect measurements used for impurity doping characterization is also described.

1.6.1 Reflected High Energy Electron Diffraction (RHEED)

Because of the great control that is afforded by MBE to the growth surface, a method of characterizing the surface during growth is highly desirable. One very powerful way to do this is to use in-situ high energy electrons in a grazing angle electron diffraction in a reflection geometry\textsuperscript{33}. The typical setup for the RHEED experiment (figure 1.13) involves an electron gun in an UHV MBE chamber, a phosphorous screen and image processing hardware and software. Typical acceleration voltages of the beam range from 10-30 keV. The electron beam grazes the
surface of the film at an angle in the range of 0.5-2.5°. The diffracted pattern that is imaged on
the phosphorous screen gives us information of the arrangement of atoms on the surface (surface
reconstruction), the crystal phase of the crystal and the smoothness and the growth rate of the
growing film all with sub-monolayer precision.

One of the most useful applications of RHEED involves the measurement of changes in intensity
of the diffracted pattern at any given point. These RHEED oscillations can be used to determine
the growth rate, alloy compositions and surface roughness of the film. The nature of these
oscillations comes from the changes in scattering that occur as a single atomic monolayer is
forming (figure 1.14). When a monolayer is complete the electron beam intensity is at a
maximum because there is no scattering from surface steps. The electron beam intensity is at a
minimum when a monolayer of the film is half-way formed because the scattering from surface
steps is maximized. By observing the time spacing of these oscillations we can determine how
long it takes for each monolayer to develop on the surface of the film and therefore the growth
rate. The growth rate of the film depends on what atoms are incorporated into the film; thus, we
can extract rough alloy compositions for ternary alloys by examining the changes in growth rate
when altering cell temperatures, or by comparing the growth rates to the binary components in
the alloy. If the growing film is too rough to see the monolayer transitions the RHEED
oscillations are said to be dampened by roughness. This dampening can give us real time
information about the crystalline quality of the film. The roughness may develop immediately or
over time; if it develops over time the number of oscillations gives a good measure of the
The crystalline phase is usually determined in RHEED by examining the symmetry of each phase and determining if it matches that of the diffracted pattern observed on the screen. This is done by measuring changes in the diffracted pattern as one rotates the angle of the film relative to the electron beam. This can be easily illustrated when comparing a hexagonal film to a cubic film. In a cubic film, one sees a repeating pattern every 90° where as a hexagonal film reveals repeating patterns every 60°. In this manner, we can also observe when there are multiple phases in the film if the repeating patterns are less than the symmetry during the intended crystalline phase.

During growth, the crystalline phase and surface reconstruction of the film can vary with growth conditions such as substrate temperature and relative pressures of the atomic beams. The atomic arrangement of atoms on the surface of the film can also be observed by examining the RHEED
pattern. Surface reconstruction is determined by the diffraction pattern because different arrangements of atoms give rise to distinct patterns in the RHEED screen. While it is challenging to identify the precise arrangement of atoms on the surface because different arrangements give rise to similar patterns, one can also observe changes in the pattern as the growth conditions change. One example of this is the evolution of the pattern as the substrate temperature changes, where one can observe transformations from a 2x1 pattern to 3x1 pattern in II-VI materials as the sample is heated.

Because of scattering to the reflected electron beam, RHEED can also be used to determine the growth mode and surface roughness of the growing film. This is accomplished by observing the length of the diffracted lines. The length of the diffracted lines is proportional to the step length that the electron beam covers. If there are no steps visible to the film, a perfectly “streaky” line is visible. As the beam sees more steps these lines begin to separate into lobes, where the length of the lobes is proportional to the distance between the steps. If the distance between steps is very small the pattern develops modulations in the otherwise streaky pattern and is said to be spotty. This gives us information about the growth mode of the film because two-dimensional growth will show the streaky pattern indicative of long distances between steps. On the other hand, three-dimensional growth will manifest a spotty RHEED pattern. Changes in growth mode can also be observed in real time if the film changes from yielding a streaky to a spotty pattern.

RHEED is a powerful tool that can be used to determine the crystal structure of a growing film. It gives us access to growth rates, alloy composition, roughness, surface reconstruction, growth
mode and crystalline phase of the growing film. Since it is performed in real time, \textit{in-situ}, it allows for corrections during the growth.

1.6.2 \textit{X-ray Diffraction(XRD)}

X-ray diffraction(XRD) is a highly effective technique capable of extracting structural information about crystals. This technique is especially useful to MEB crystal growers because it is non-destructive, requires a relatively small sample size and provides some of the most important information needed for crystal growth. Some of the information available from XRD includes lattice constant (or mismatch to substrate), misorientation, dislocation content, mosaic spread, inhomogeneity, curvature, strain and relaxation and thickness of various layers\textsuperscript{34}.

Typical laboratory XRD setups, such as the one used here, produce x-rays by accelerating high energy electrons to a metal target, usually copper. A schematic of a standard laboratory setup is shown in figure 1.15a, where the different angles and optics that can be adjusted are shown. In the XRD scan presented in this dissertation a Bruker D8 discover with a da Vinci configuration was used (figure 1.15b). Electrons were accelerated to about 40KeV before hitting the copper target. Due to the high energy of the electrons core shell high energy excitations take place producing x-ray light. K\textsubscript{α1} and K\textsubscript{α2} are the two primary high energy excitations that are often used for copper and are associated with 2p shell to 1s shell transitions. In our setup after the x-ray light is produced it moves through a beam conditioning silicon crystal that isolates the K\textsubscript{α1} light which has a wavelength of $\lambda=0.154056$ nm. After the light is conditioned it passes into a variable slit and a variable collimator to shape the beam size. The light then diffracts off the sample surface and the diffracted light is collected in one of three ways. In the double crystal
setup(XRD), light goes through a variable slit before the scintillator detector equal to the beam slit. Since there is no conditioning of the signal, analysis associated with crystal quality can be performed. In the triple bounce setup(HR-XRD), an analyzer crystal is placed before the scintillator detector. This has the effect of increasing angular resolution significantly at the expense of losing broadening information. This setup is used to accurately determine the positions of the Bragg reflections for thickness as well as lattice constant measurements. In the third setup, a Vantec two-dimensional detector is placed instead of a single point scintillator. This setup has the unique advantage of giving information on a very large area of reciprocal space at the expense of resolution; it is utilized when the crystal structure of the film is in question and needs to be determined. Once the optics are in place we can begin to extract structural information from the film.

The simplest and most useful description of diffraction was obtained by Bragg\textsuperscript{35}. In this description, constructive interference occurs when:

\[ n\lambda = 2d \sin \theta \]  

(1.16)
where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of light (here \( \lambda = 0.154056 \text{ nm} \)), \( d \) is the planar distance of the diffracting plane, \( \theta \) is the angle of incidence and diffraction is relative to the diffracting plane. It would seem from Bragg’s law that one would get single diffracted lines from each diffraction; however, there is broadening from many factors that influence the width of each of the diffracted lines. This width is known as the rocking curve width which is a range where each diffracted peak occurs. In a theoretically perfect crystal the width of the rocking curve is determined only by thickness and the nature of the radiation diffracted on the sample. In real grown crystals, there are many factors that influence the broadening of a diffracted peak; these are summarized by the following formula\(^{36}\):

\[
[B_m(hkl)]^2 = [\beta_0(hkl)]^2 + [\beta_L(hkl)]^2 + [\beta_r(hkl)]^2 + [\beta_{\text{instrument}}(hkl)]^2 + [\beta_{\text{dislocations}}(hkl)]^2 \tag{1.17}
\]

where \([B_m(hkl)]^2\) is the measured rocking curve full-width at half maximum (FWHM) for the \( hkl \) reflection; \([\beta_0(hkl)]^2\) is the natural rocking curve width of a perfect crystal of the sample being studied; \([\beta_L(hkl)]^2\) is the broadening due to the crystal thickness; \([\beta_r(hkl)]^2\) is the broadening due to curvature; \([\beta_z(hkl)]^2\) is broadening due to strain; \([\beta_{\text{instrument}}(hkl)]^2\) is the broadening due to the experimental setup; and \([\beta_{\text{dislocations}}(hkl)]^2\) is the broadening from defects in the crystal. It is evident that there are many factors contributing to the rocking curve widths, so a complete analytical extraction of any of the parameters from rocking curves is difficult. Yet, by keeping all other parameters constant we can extract one or more parameters from the sample. Simple qualitative comparisons can also be made by keeping all parameters such as thickness and composition of the crystal fixed when preparing the sample and comparing the FWHM.
Hence, we can apply Bragg’s law to determine the spacing between atomic planes by rearranging equation (1.16) to:

\[
d = \frac{0.154056}{2 \sin \theta}
\]

(1.18)

where \(d\) is spacing between planes of the material being measured. This \(d\) value translates into lattice constant (\(a\)) if the film is relaxed (figure 1.17a). Because of small changes in the angles measured for a Bragg reflection as well as the alignment of the XRD optics, it is often more useful to measure the deviation of the grown film from that of the substrate. This deviation from the substrates lattice constant is known as mismatch and is defined thus:

\[
m = \frac{a_{\text{layer}} - a_{\text{substrate}}}{a_{\text{substrate}}} = \frac{a_l - a_{s}}{a_{s}} = \frac{\Delta a}{a}
\]

(1.19)

where \(m\) is the mismatch in \%, and \(a\) is the measured \(d\) spacing for the layer and the substrate. If the film is not relaxed there are additional complications due to strain-related distortion of the crystal. In cubic films the main strain-related distortion that occurs is a tetragonal distortion to the lattice. In this case, it is sufficient to take the average of the in-plane, or parallel, lattice constant (\(a_{\parallel}\)) and the out of plane, or perpendicular, lattice constant (\(a_{\perp}\)):

\[
a_{\parallel}^r = \frac{a_{l} - a_{\perp}}{2} \times 100\%
\]

(1.20)
where $a_T$ is the lattice constant for the undistorted layer. For zinc blende crystals, the lattice constants can be extracted from the d values obtained from the (004) Bragg reflection for $a_{\parallel}$ and (224 or 115) Bragg reflections for $a_{\perp}$. An additional parameter that can be extracted from these two measurements is the degree of relaxation in the film ($R$):

$$R = \frac{a_\parallel - a_s}{a_T - a_s} \times 100\%$$  \hspace{1cm} (1.21)$$

Additionally, we can also determine the amount of strain in the perpendicular direction film utilizing a similar formulation:

$$\varepsilon_\perp = \varepsilon_{zz} = \frac{a_\parallel - a_T}{a_T}$$  \hspace{1cm} (1.22)$$

where $\varepsilon_\perp$ is the perpendicular strain in the layer. Once the $a_T$ value of the layer is obtained we can now determine the composition of the layer from the stoichiometry of the elements contained in the sample. This can be estimated to good precision using Vegard’s law for binary compounds:
Chapter 1: Introduction

\[ a_{A_xB_{1-x}} = x a_A + (1-x) a_B \]  \hspace{1cm} (1.23)

where \( a_{A_xB_{1-x}} \) is the measured \( a_r \) value and \( x \) is the composition expressed in percentage of component A. For alloys with three components (TA) such as ZnCdSe this method is still useful, but we must assume one of the elements to 50% stoichiometry, as is often the case with semiconductor films:

\[ a_{A_xB_{1-x}C} = x a_A + (1-x) a_B \]  \hspace{1cm} (1.24)

where the stoichiometric percentage of C is ignored. For alloys with four components (QA) such as ZnCdMgSe, or for TA whose C component does not have 50% composition, Vegard’s law is not enough to determine composition and an additional data point is necessary to calculate composition. This is typically done by using photoluminescence in addition to XRD.

The next important parameter that can be extracted from XRD measurements is the thickness of the layers in a heterostructure. Although, using XRD for thickness is an approximation and other techniques such as x-ray reflectivity (XRR) described later are more accurate, one can still extract very good estimates of thickness if XRR is not available. The first thickness calculation one can perform is for so-called Pendellösung fringes. These fringes result from an interference effect at the interfaces in the layers and their presence and shape can be a good qualitative indication that the two interfaces of the layer are smooth. In addition, to interface roughness one can extract the thickness of the film from their period34:

\[ \text{thickness} = t = \frac{\lambda(n_2-n_1)}{2 \sin \theta_1 - \sin \theta_2} \]  \hspace{1cm} (1.25)

where \( t \) is the thickness of the film, \( \lambda \) is the x-ray wavelength, \( n \) is the order of the fringe and \( \theta \) is the measured angle for each fringe. Additional accuracy can be gained by taking as many fringes as are available and examining the slope of the curve (figure 1.17b). The angular values for these
fringes are usually obtained from coupled 2θ-ω scans because of the additional angular resolution. This method of thickness estimation can also be applied to any repeating structure in a heterostructure. This is because repeating structures such as superlattices have their own rerated interference effects. These interference effects are known as superlattice fringes and their sharpness can be a good indication of the quality of all the interfaces in the repeating structure. The angular separation of the superlattice fringes also gives us an accurate measurement of the thickness of one of the repeating units. We can extract the thickness of this repeating unit using formula 1.18 in the same way we did for Pendellösung fringes.

Figure 1.18:(a) X-ray reflectivity scan of ZnCdSe/MgSe superlattice on an InP substrate showing the Kessing fringes for a ZnCdSe buffer (period 1) and the period of the superlattice (period 2). The amplitude of the fringes is determined from the electron density contrast and the decay slope of the signal indicates the roughness in the sample.
Although there are several more parameters that can be extracted from XRD we will treat those individually in the following chapters when they are applied. For the most part the structural parameters presented above are used in nearly every film grown by MBE.

1.6.3  *X-ray Reflectivity (XRR)*

Another technique that has become common in semiconductor crystal growth is x-ray reflectivity (XRR). This technique can be used to extract the density, thickness and surface and interface roughness. The experimental setup is the same as was outlined above for double crystal XRD with a small slit size typically 0.05 mm to 0.2mm both before the sample and before the detector to increase the angular resolution. The technique involves measuring the intensity of the x-ray beam at grazing angles. The measurement of density is not as sensitive as the composition values we can achieve with XRD. Roughness estimated from XRR gives similar values to those achieved with other techniques such as atomic force microscopy (AFM), though the roughness values tend to be larger. The three parameters of roughness, density and thickness are best extracted using kinematic theory simulations, but very good estimates for thickness can be extracted from simple estimates (figure 1.18). Because this technique is not sensitive to diffraction effects it can give a more accurate measurement of thickness than XRD. When the x-ray beam passes through the sample interference fringes known as Kiessig, fringes are evident in the measurement. Kiessig fringes give thickness using the same formula derived from Bragg’s law in formula 1.18. Unlike XRD the technique is not sensitive to the crystal structure but simply the roughness of the film. It is sensitive to film thicknesses below 100nm with increasing accuracy as the thickness becomes smaller. Overall XRR provides a nondestructive method to extract very accurate thicknesses as well interface and surface roughness.
1.6.4 Photoluminescence (PL)

Photoluminescence (PL) is the spontaneous emission of photons by a material after optical excitation. PL is a nondestructive technique that provides important optical and electronic information about the material. It can be used to probe several electronic rather than mechanical properties of the sample such as bandgap, quality of the samples, donor and acceptor states, deep level defects and spin processes. To understand the process more formally one needs to consider the mechanism of photoluminescence.

In the measurements presented here a relatively simple setup was used to perform steady-state photoluminescence measurements. The experimental setup included a 325nm Milles Griot HeCd laser with a power rating of 25 mW. Directly in front of the laser was a monochromatic filter to make certain that only the desired wavelength was emanating from the laser source. Subsequently, a variable neutral density filter wheel was placed in the laser beam’s path in order to carry out intensity dependence studies. The optical densities of the filter wheel varied from 0 to 3. A cylindrical lens was then used to focus and direct the laser beam horizontally onto the sample. The sample was afterwards exposed to the laser either in a room temperature sample holder, or inside a cryostat with a temperature gauge. Most samples were measured at both 77K and room temperature. The resultant emission was then focused with the use of two lenses onto an Ocean Optics spectrometer.
The most important parameter extracted from PL measurements is that of the bandgap of a semiconductor. To understand how this is possible we need to examine some of the basics of electronic structure. All extended solids have discrete energy bands for their electrons that arise from the loose binding nature of electrons to individual atoms within the solid. Electrons of a lower energy occupy the valence band while electrons of higher energy may exist in the conduction band (figure 1.19). The valence band arises from electrons that occupy bonding sites and are thus localized at the atom sites, while the conduction band represents non-bonding energy states and its electrons are delocalized throughout the solid. When the difference between the conduction and valence bands is zero a conductor ensues allowing electrons to flow freely though the lattice, such as what happens in metal. When the difference is not zero, an energy gap (E_g) arises where electrons are not allowed. When a photon whose energy is greater than E_g is incident onto the material, the photon can be absorbed raising the energy of an electron from the valence band to the conduction band. After this, the electron loses excess energy until it comes to

Figure 1.19: Schematic for the various processes that take place in photoluminescence spectroscopy. The common radiative recombination mechanisms that can take place in a semiconductor include (a) conduction band to valence band, (b) donor to valence band, (c) conduction band to acceptor level, (d) donor to acceptor level, (e) deep level recombination
rest at the lowest energy level (thermal relaxation). Because the electron that was promoted leaves a hole in the valence band, a lower energy state in that band is vacant. The electron then may spontaneously relax back to the valence band releasing an energy equal to $E_g$ (figure 1.19a). The rate of transitions that occurs is determined by product of the density of electrons in the upper state ($n_u$), the density of empty lower energy states ($n_l$) and the probability for 1 electron per unit volume to make a transition to the lower state per unit volume $^{39}$:

$$R = n_u n_l P_{n \rightarrow l}$$

(1.26)

Because of the relaxation to the lowest energy level in the conduction band, the spectrum from photoluminescence produces a sharp peak at the energy gap.

Now let us consider the relationship between the absorption and emission in PL. The relationship between the light incident on the sample and that absorbed can be understood thus:

$$I = I_0 (1 - R)$$

(1.27)

where $I$ is the light absorbed though the sample, $I_0$ is the intensity of the light before it reaches the sample and $R$ is the fraction of reflected light. Absorption decays through the sample because as photons are absorbed there are less photons available; this relation can be summarized by the following equation:

$$I(x) = I_0 e^{-\alpha x}$$

(1.28)

where $I_0$ is the intensity of light hitting the sample, $x$ is the depth in to the sample and $\alpha$ is what is known as the optical absorption coefficient, which varies from material to material.
Although the bandgap emission is the primary information being sought using PL, it is not the only emission that takes place. There are several other emissions within the energy gap that occur due to several material properties. One such emission takes place because of doping of the semiconductor. In n-type doping the donor electrons in the dopant band can undergo radiative recombination with the holes in the valence band (figure 1.16b). This creates a peak that is equal to the energy of the band-gap minus the energy level of the donor, $h\nu=E_g-E_d$. In p-type semiconductors exited electrons can undergo a transition to the acceptor energy level of the dopant rather than the valence band in a similar mechanism (figure 1.19c). In practice these transitions are usually observed as a broadening of the energy gap peak on the lower energy side of the spectrum. Other impurities can also give rise to transitions like those produced via the

![Photoluminescence spectra of a ZnCdSe sample showing the bandgap emission and the deep level emission.](image)

Figure 1.20: Photoluminescence spectra of a ZnCdSe sample showing the bandgap emission and the deep level emission.
doping mechanism. These transitions are usually observed as sharp peaks well below the energy gap, known as shallow levels. Crystalline defects in the sample can produce intermediate states within the bandgap that, when recombination occurs, produce light. The light from these transitions tends to be very broad, well-below the energy gap, and known as deep levels (figure 1.20). Dislocation networks at the interface between two materials that are lattice-mismatched give rise to similar deep emissions. Because deep emission is a product of a breakdown in the crystalline structure of the sample, it can be a good indicator of the crystalline integrity of the sample being probed.

1.6.5 Contactless Electro-reflectance

Contactless modulated optical spectroscopy of semiconductors is a useful way to evaluate the electronic structure of MBE grown samples. Contactless electro-reflectance is a modulation technique applied to reflectance without any contacts applied to the sample. As in all

Figure 1.21: Contactless electroreflectance spectra of an intersuband II-VI test structure showing electronic transitions.
modulation spectroscopy, a low frequency oscillatory signal gives $\Delta R/R$ of the reflectance. This derivative-like function allows us to see resonances corresponding to band to band transitions in the sample. The detected transitions can then be mapped with the aid of electronic structure simulations to the corresponding intersubband transitions in the sample. This technique is especially effective when extracting energy levels in quantum well structures with most features visible in the spectra even at room temperature.

The power of this technique can be seen in the CER spectra taken at room temperature presented in figure 1.21. We can see various transitions that are present in the quantum well system. These transitions can be mapped to intersubband energy levels in the well. These energy levels are typically hidden in other spectroscopy techniques such as PL and unmodulated absorption measurements. Knowing these transitions aid the design of ISB devices presented in this thesis, giving us the position of energy levels, conduction band offset and other parameters needed for their design.

1.6.6 Fourier Transform Infrared Spectroscopy

Another more direct method of probing ISB transitions in quantum well structures such as quantum cascade lasers and detectors is Fourier transform infrared(FTIR) spectroscopy. This technique has been used extensively to study absorption in many applications. At the heart of FTIR spectroscopy is the Michelson interferometer$^{42}$ that allows us to extract accurate spectroscopy data quickly. The Michelson Interferometer consists of a beam splitter onto a fixed mirror and a moving mirror that translate back and forth. Radiation from the source separates into two beam paths: one that reflects on the fixed mirror and one that reflects on the moving
mirror. The two beams are seen by the detector simultaneously and then, depending on the wavelength of light, constructively or destructively interfere. The wavelengths then separate with the use of a Fortier transform algorithm\textsuperscript{43}.

In the case of ISB absorption in a quantum well, absorption only happens when the electric field is perpendicular to the growth direction. A background spectra is first collected to remove any atmospheric and absorption from the optics. Because of this, one can remove the non ISB transition signal from the spectrum by subtracting the transverse electric(TE) from the transverse magnetic(TM) light by using a polarizer. The samples were prepared for this measurement by polishing 45° facets to create an attenuated reflectance cavity within the sample so that multiple passes can increase the weak signal from the ISB energy levels. The position of these energy levels can be used to modify the growth conditions or design of the structure to tailor the emission or detection wavelengths of ISB devices.

1.6.7 Hall Effect

Hall effect is widely used to determine the carrier characteristics of materials. The primary parameters extracted from the Hall effect are free carrier concentration, carrier mobility, carrier type and resistivity. Hall Effect measurements are based on the fact that as a current flows through a conductor perpendicular to a magnetic field, the magnetic field exerts a transverse force on the moving carriers. In response to this Lorentz force electrons, and force exerted by the internal electric field electrons, are defected. The Lorentz force is given by:

$$F_L = -q[E + v_d \times B]$$

(1.29)
where $v_d$ is the drift velocity, $q$ is the elementary charge ($1.602 \times 10^{-19}$ C) and $B$ is the applied magnetic field. For an n-type semiconductor (figure 1.22a) with an applied current, carriers would be deflected in the negative $y$ direction accumulating charge. This charge results in a Hall voltage ($V_H$) whose magnitude is equal to:

$$V_H = \frac{I_x B}{q nt} \tag{1.30}$$

where $t$ is the thickness of the sample, and $n$ is the bulk majority carrier density. To determine the sheet carrier density, $n_s = nt$, thus:

$$n_s = \frac{I_x B}{q |V_H|} \tag{1.31}$$

So, if we measure the Hall voltage $V_H$ for fixed $I_x$, $B$ and $q$ we can determine the bulk and sheet majority carrier concentrations in semiconductors. For p-type carriers the sign of the Hall voltage would be positive and negative for n-type carriers. The measurements in this dissertation were performed using the van der Pauw (VdP) configuration. This method has the advantage of relatively simple sample preparation and the ability to measure sheet carrier concentration and

![Schematic Diagram of Hall effect in an n-type semiconductor and the van der Pauw measurement configuration.](image)

Figure 1.22: Schematic Diagram of Hall effect in an n-type semiconductor (a) and the van der Pauw measurement configuration (b).
sheet resistivity($R_s$) simultaneously. $R_s$ can be determined in the VdP configuration by measuring the voltage and current across the various contacts shown in figure 1.22b. The two characteristic resistances in this configuration are defined as:

$$R_A = \frac{V_{43}}{I_{12}} \quad \text{and} \quad R_B = \frac{V_{14}}{I_{23}}$$

(1.32)

where the numbers represent measurement across the numbered contacts in the configuration.

These characteristic resistances can be used to solve $R_s$ by the van der Pauw formula:

$$e^{-\pi R_A/R_s} + e^{-\pi R_B/R_s} = 1$$

(1.33)

From the value of $R_s$ electrical resistivity can be solved for the bulk using:

$$\rho = R_s t$$

(1.34)

Once we have $n_s$ and $R_s$ the calculation of Hall mobility($\mu$) is from the equation:

$$\mu = \frac{1}{q n_s R_s}$$

(1.35)

The measurements presented in this dissertation were usually carried out using a Lakeshore Hall Measurement system or a physical property measurement system(PPMS) for low temperature measurements. All measurements were done within the VdP configuration utilizing silver contacts for Bi2Se3 samples or indium contacts for II-VI materials.

1.7 Outline of Thesis

Chapter 1 presents background information into the modeling, growth and characterization techniques used in this dissertation. This information is critical to understanding the subsequent chapters.

Chapter 2 describes the basic growth of high quality II-VI material lattice matched to InP. It also examines the growth of the Bi2Se3.
Chapter 3 discusses growth interruptions and their use in II-VI quantum cascade emitter materials. A complete discussion of the implementation and device performance improvements is presented here.

Chapter 4 illustrates applications of growth interruptions in other II-VI devices. These applications include progress towards the realization of II-VI green gap optically pumped disk lasers. Additionally, the realization and performance of novel intersubband quantum cascade detectors (QCDs), broadband QCDs and monolithic hybrid III-V/II-VI QCDs are discussed.

Chapter 5 catalogs the growth and characterization of wide bandgap ZnCdSe/MgSe digital alloys as a viable alternative to ZnCdMgSe. Included is an in-depth discussion of the growth and properties of the digital alloy as well as details for their modeling and use.

Chapter 6 describes the growth and characterization of Bi$_2$Se$_3$ and II-VI heterostructures. We first look at wurtzite phase ZnSe, ZnCdSe and ZnCdMgSe bulk material on Bi$_2$Se$_3$. Then, we examine growth and characterization of Bi$_2$Se$_3$/ZnCdSe and Bi$_2$Se$_3$/CdTe multilayers and superlattices.

Chapter 7 addresses the use of Bi$_2$Se$_3$/CdTe as a van der Waals virtual substrate for multiple quantum well structures on sapphire substrates.

Chapter 8 concludes the findings of this dissertation with suggestions for future research.
Chapter 2: MBE Growth of II-VI and Bi\textsubscript{2}Se\textsubscript{3} Materials

2 MBE Growth of II-VI and Bi\textsubscript{2}Se\textsubscript{3} Materials

To research any material system for device application or physical investigation the growth of all parts must be well understood. We first describe the Zn\textsubscript{x}Cd\textsubscript{1-x}Se/Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-y-x}Se semiconductor material system. Subsequently, we detail the growth of three bulk materials which will form the base of all presented structures. These include Zn\textsubscript{x}Cd\textsubscript{1-x}Se, Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-y-x}Se semiconductor alloys lattice matched to the InP substrate and the binary Bi\textsubscript{2}Se\textsubscript{3} topological insulator.

2.1 ZnCdSe/ZnCdMgSe Material System

Initially explored as a visible light emitting material system, the Zn\textsubscript{x}Cd\textsubscript{1-x}Se/Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-y-x}Se on InP is a highly versatile wide-bandgap zinc blende semiconductor system useful for important device applications. Although lack of a well-behaved p-type dopant has limited the performance of p-n devices to date, intersubband unipolar (n-type only) and optically pumped\textsuperscript{44} devices remain very attractive. In this system, Zn\textsubscript{x}Cd\textsubscript{1-x}Se is utilized as the low bandgap well material with a lattice matched bandgap of 2.11eV\textsuperscript{45}. Zn\textsubscript{x}Cd\textsubscript{1-x}Se can be grown in high quality on InP with special buffer treatments at the heterovalent interface\textsuperscript{46}. Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-y-x}Se is utilized as the barrier system with lattice matched room temperature bandgaps ranging from 2.11-3.52eV\textsuperscript{15}. This barrier has been grown in high quality\textsuperscript{47,48} with low defect densities\textsuperscript{49} lattice matched to InP. Additionally, both well and barrier compositions can be n-type doped using ZnCl\textsubscript{2} as the dopant source\textsuperscript{50}. In optically pumped devices, these two materials allow for quantum well emission...
energies that span the entire visible spectrum. In intersubband device applications, a large conduction band offset (CBO) of up to 1.12 eV makes them attractive for short wavelength mid-IR devices and room temperature terahertz devices.

As shown in Figure 2.1, the lattice constant of ZnxCd(1-x)Se and ZnxCdMg(1-y-x)Se alloys can be adjusted by varying the composition to be lattice matched to InP. The zero-mismatch position is shown by a dotted line, and the ternary lines, including bowing parameters between the ZnSe, CdSe and MgSe binary components, are shown by solid lines. We can see that the bandgap of ZnMg(1-x)Se is linear, CdMg(1-x)Se is nearly linear (0.2), and ZnCd(1-x)Se alloy has a bowing parameter of 0.3. As we can infer from the graph, and samples grown by our group (shown in Figure 2.1: 77K bandgap vs. lattice mismatch to InP of ZnxCd(1-x)Se and ZnxCdMg(1-y-x)Se alloys.
circles), it is possible to grow InP lattice matched Zn$_x$Cd$_{y}$Mg$_{(1-y-x)}$Se alloys with a wide range of bandgaps.

It is important to consider that unlike Si and III-V semiconductors, these materials have not to date achieved commercial success. It is also evident that there are no high quality native substrates for II-VI materials in this lattice constant range. Because of this, commercially available III-V and sapphire substrates are typically used for the growth of these materials (InP in this case). The growth of these materials on these substrates involves heterovalent interfaces that are thermodynamically unstable; therefore, precise control of the interface between the substrate and the grown film must be achieved.

2.2 ZnSe Heterovalent Interface

ZnSe growth on GaAs is the most well studied II-VI/III-V heterovalent interface to date; therefore, it is useful to understand it while delving into the growth of alloys on InP. In this interface, it was found that the surface stoichiometry is of paramount importance in forming a good ZnSe/GaAs interface$^{23,53}$. Surface energy calculations show this interface can proceed by

![Figure 2.2](image.png)

Figure 2.2 (a) relevant compounds involved in II-VI/III-V interface. (b) The number of valence electrons for atoms (black) and bonds (red) involved in the GaAs/ZnSe. (c) Arrangement of atoms in an electronically balanced heterovalent GaAs/ZnSe interface.
the desired 2d growth mode as the surface energy for ZnSe is much lower than that of GaAs. As a first approximation, the application of electron counting method (EMC) reveals that a mixed stoichiometry of Ga-Se and Zn-As bonds will yield a thermodynamically stable surface (figure 2.2c). Growth studies confirmed this when observing that growth Ga rich 4x2 yielded very defective films, with large amounts of Ga₂Se₃ interfacial compounds. On the other hand, growth on the As rich β₂(2x4) reconstruction could achieve a balanced mixed stoichiometry. In theoretical work using DFT with a local density approximation, Kley and Neugebauer calculated that all abrupt interfaces are thermodynamically unstable. They also calculated the possible arrangements of GaAs/ZnSe mixed interfaces and the c(2x2) interface as the most stable, in good agreement with the simple electron counting model. However, the GaAs/ZnSe c(2x2) interface is experimentally difficult to reproduce consistently, and growth of ZnSe on the β₂(2x4) reconstruction has become the surface of choice for ZnSe. Further modification of the growth procedure by exposing the surface to Zn before GaAs growth reduces Ga-Se reactions that take place in the trenches of the β₂(2x4) reconstruction, reducing Ga₂Se₃ associated defects.

2.3 Growth of II-VI Alloys on InP by MBE

To grow ZnₓCdₜ₋ₓSe and ZnₓCdₓMgₓ₋ₓ₋ₓSe alloys on InP, similar treatments need to be performed in order to deal with the effects of the heterovalent interface. In the case of InP the substrate is prepared for II-VI growth by first growing a thin InₓGaₓ₋ₓAs layer lattice matched to InP(x=0.47) with the appropriate β₂(2x4) reconstruction. The purpose of the InGaAs buffer is to form a smooth surface and to allow us to control the surface stoichiometry better.
2.3.1 Pre-growth Preparation

To ensure a smooth surface for epitaxy and to prevent contamination associated with the transfer between a III-V and II-VI chamber, special preparation is necessary when growing II-VI alloys on III-V substrates. Substrates are first mounted onto a reusable molybdenum block using indium to bond the substrate to the block. Because II-VI alloys are contaminants in a III-V chamber, steps need to be taken to ensure the block is free of any II-VI material prior to mounting. This is done by first removing the previous growths indium in a concentrated hydrochloric acid bath. Then the block is rinsed and the II-VI material is etched in a bromine methanol (~20% bromine) bath for 10 minutes. Subsequently, the surface of the block is etched further by dipping in aqua regia (HCl:HNO₃) three times for 20 seconds. Next, the block is rinsed in water for 10 min followed by methanol to remove any residual chemicals from the etching processes. At this point the block is ready for the substrate to be mounted. The substrate is mounted by melting indium on the surface of the block and smearing the substrate until there is strong bond. After the substrate is attached, the block is loaded into a dedicated loading chamber and pumped down to a pressure of ~1x10⁻⁹ and is all set to be introduced into the III-V chamber.

Substrates used here contain either a grown oxide or a native oxide, but are otherwise “epi-ready”. This means that although no further chemical treatments need to be performed on the substrate the oxide must be removed before growth can begin. For InP, this is done in a chamber dedicated to III-V materials. In this procedure, the sample is first heated to approximately ~250°C and then exposed to an arsenic overpressure of ~1.5x10⁵. This prevents the indium in the substrate from condensing as the phosphorous is desorbed from the substrate surface. The sample is then slowly heated to a temperature 500°C. As the sample is heated a (2x4) reconstruction
becomes visible. To ensure that full oxide removal has occurred the transformation of the (2x4) reconstruction to that of a metal rich (4x2) reconstruction is observed. Immediately after the (4x2) reconstruction becomes visible, the substrate is subsequently cooled by 20˚C and is ready for the growth of In_{x}Ga_{1-x}As. At this point an In_{x}Ga_{1-x}As buffer layer is grown. Although II-VI alloys have been grown on InP directly\textsuperscript{55} it was found that a thin In_{x}Ga_{1-x}As layer improves the surface smoothness and makes it simpler to prepare the $\beta_2$/(2x4) surface reconstruction needed for II-VI growth\textsuperscript{56}.

Once the In_{x}Ga_{1-x}As buffer is grown the sample is then transferred via an UHV transfer mechanism to a chamber dedicated to the growth of II-VI materials. At this point the heterovalent interface needs to be prepared to prevent defects associated with the valency imbalance. Like in the growth of ZnSe, it was found that exposure to zinc at a nominal temperature of ~170˚C before any II-VI growth occurs creates a stable surface by preventing the formation of In$_2$Se$_3$ or Ga$_2$Se$_3$ interfacial compounds. In order to begin the Zn$_x$Cd$_{(1-x)}$Se growth it was found that a thin layer grown at this low temperature (known as the low temperature buffer or LTB) greatly improved the quality of the material\textsuperscript{48}. Once both these steps are taken the sample temperature is raised to an optimal nominal temperature of 270˚C and the remaining II-VI structures can be grown. In the case of Zn$_x$Cd$_y$Mg$_{(1-y-x)}$Se alloys, a thin Zn$_x$Cd$_{(1-x)}$Se layer grown at the 270˚C was found to improve the material quality\textsuperscript{48}; direct low temperature growth of Zn$_x$Cd$_y$Mg$_{(1-y-x)}$Se was found not to be favorable.
2.3.2 Further improvements of the ZnxCd(1-x)Se Low Temperature Buffer (LTB)

Two modifications are presented here to the low temperature buffer (LTB) to further improve the quality of ZnxCd(1-x)Se based structures. These include changing the stoichiometry of the low temperature ZnxCd(1-x)Se buffer and replacing it with a tellurium buffer.

Tellurium pre-exposure (Te start) was attempted by many workers in the GaAs/ZnSe interface and yielded some of the best critical thickness values of ZnSe reported in the literature. This improvement was attributed to a surfactant effect from tellurium\textsuperscript{57}. Despite first principles DFT calculations stating that interdiffusion would be suppressed at the Te/GaAs interface\textsuperscript{20}, Ga\textsubscript{2}Te\textsubscript{3} related stacking faults were found in the grown material\textsuperscript{58}. However, there are clear advantages of a one monolayer interface and optical quality of Te start ZnSe films is promising. In ZnxCd(1-x)Se, we find that good optical quality films, comparable to the best with a low temperature buffer, are also achieved (figure 2.3). Despite the promising optical results, defect density measurements on these films show that related staking faults remain a problem for Te start films as they did for ZnSe.

![Figure 2.3: 77K Photoluminescence spectra of Te start ZnCdSe sample with a full-width at half maximum of 22meV and no observable deep levels.](image-url)
A second modification to improve this interface was to modify the low temperature buffer layer stoichiometry to get a better low temperature buffer, with improved lattice matching. One problem with the original low temperature buffer is that the sticking coefficient changes for the two growth temperatures used for ZnxCd(1-x)Se. While the sticking coefficient of Zn has been found to be in unity at relevant temperatures, the sticking coefficient of Cd varies from the low temperature buffer temperature of 170°C to 270°C. The change of the sticking coefficient changes the composition of the films at low temperatures away from lattice matching thus degrading the roughness of the film. This can be seen by examining the dampening of RHEED oscillations during the growth of the low temperature buffer. We can see in figure 2.4a that dampening of the RHEED intensity oscillations at the growth temperature is much lower than it is for the low temperature buffer, indicating that growth at low temperatures is much rougher. However, if we account for the change in sticking coefficient for cadmium, and correct for it by reducing the Cd temperature, we can decrease the dampening. In figure 2.4b we also see that the growth rate changes at the two temperatures. We find that we can get nearly the same growth rate for both temperatures by adjusting the cadmium temperature by 1°C indicating that we

Figure 2.4: (a) RHEED Oscillation dampening as a function of cadmium temperature, we can see dampening occur much slower when a 1°C adjustment is made. (b) Change in growth rate as a function of cadmium temperature at the two growth temperatures. (c) FWHM of 2θ-ω x-ray diffraction peaks for ZnxCd(1-x)Se and ZnxCdyMg(1-y-x)Se samples.
achieve the same lattice matched stoichiometry at 170°C, as we do for 270°C. In figure 2.4c we see that the FWHM of 2θ-ω XRD scans is reduced for lattice matched samples when decreasing the cadmium temperature by 1°C during the low temperature buffer layer growth. The modification of the substrate temperature is shown to be an excellent way of improving the initial surface to epitaxy of ZnxCd(1-x)Se based structures.

2.3.3 ZnxCd(1-x)Se and ZnxCd_yMg_{(1-y-x)}Se Bulk Calibration

Before a device based on the ZnxCd(1-x)Se /ZnxCd_yMg_{(1-y-x)}Se multilayer material system can be grown, we need to evaluate the properties of the constituent bulk materials. The main properties that interest us in these bulk calibration samples are lattice constant, composition, bandgap and crystal quality, and the dopant concentration, when doped layers are grown. To evaluate these properties, fully relaxed ~1µm thick calibrations samples of ZnxCd(1-x)Se and ZnxCd_yMg_{(1-y-x)}Se are grown and characterized.

To achieve the highest quality films in epitaxy it is important to suppress the formation of misfit dislocations due to differences in lattice constant. The best way to do this is to increase the

Figure 2.5: 2θ-ω x-ray diffraction scan of the (004) reflection(a) and the (224) reflection(b) used to calculate the lattice constant and composition of ZnxCd(1-x)Se and In_xGa_{(1-x)}As in samples. (c) Photoluminescence spectra at 77K of the same sample.
critical thickness to infinity by preparing an alloy that has the same atomic spacing as its substrate template. At the optimum growth temperature selenium rich ZnxCd_{1-x}Se (Se to metal ratio of ~10), we can achieve lattice matched films with a beam equivalent pressure (BEP) ratio of Zn to Cd (fCd/FZn) of 2.0. For ZnxCd_yMg_{(1-y-x)}Se the BEP ration will depend on the bandgap required for a particular device application. Typical BEP of metal (fSe / (fMg + FZn + FCd) to selenium range from 5-10, but the best quality material is usually achieved with a BEP of 6-7. It is important to note that solid sources such as Zn, Cd, Mg and Se deliver different fluxes from one growth to another due to changes in surface area as the material changes shape. This means that the BEP that is achieved at a given source temperature differs over time. Because of this variance, calibration samples need to be grown continuously to make certain that the lattice matched condition has not changed. In figure 2.5 we can see how this was accomplished utilizing XRD and PL spectra for a ZnxCd_{(1-x)}Se samples. The (004) gives us the out of plane lattice constant and the (224) gives us the in-plane lattice constant. In this sample, we note that both are the same indicating that the film is fully relaxed, as is to be expected for 1µm thick samples. We can directly extract the composition from XRD using Vegard’s law once the lattice constant of the relaxed film is determined. In figure 2.5c we can see the PL spectrum for the same sample. The composition and therefore lattice constant can also be extracted from this spectra by using the bandgap bowing parameter of 0.3 for the ZnxCd_{(1-x)}Se. For ZnxCd_yMg_{(1-y-x)}Se; since there are two unknowns for the composition, both XRD and PL are needed to determine composition. We first determine the lattice constant using Vegard’s law with a combination of (004) and (224) scans (figure 2.6a,b) and the measured PL bandgap of the sample. Vegard’s law for ZnxCd_yMg_{(1-y-x)}Se is defined as:

\[ a(x, y) = 5.667x + 6.076y + 5.89(1 - y - x) \] (2.1)
where \( a \) is the lattice constant and \( x \) is the fraction of Zn and \( y \) is the fraction of Cd in the sample and the numbers are the respective lattice constants for Zn, Cd and Mg. The equation derived from the bowing parameters for the Zn\(_{x}\)Cd\(_{y}\)Mg\(_{1-x-y}\)Se at 10K bandgap \( E_g \) is \(^{60}\):

\[
E_g(x,y) = -0.35xy - 0.83y - 1.87y + 3.65
\]  

(2.1)

We can now solve both these equations simultaneously using the measured lattice constant from XRD and the measured bandgap from PL measurements to determine the Zn\(_{x}\)Cd\(_{y}\)Mg\(_{1-x-y}\)Se composition.

To evaluate the quality of the crystal most samples are characterized by XRD, PL, Nomarski optical microscopy and XRR. XRD quality is evaluated by comparing the FWHM of rocking curves and 2θ-ω scans of samples with changing growth conditions. With PL scans we examine the presence of deep levels as well as the FWHM of the band to band transitions. For example, PL in good quality samples, such as the one shown in figure 2.5c, should show no detectable deep levels at either room temperature or 77K PL spectra. The FWHM of Zn\(_x\)Cd\(_{1-x}\)Se should be below 21 meV and the best samples have FWHM below 19meV. Nomarski optical micrographs are very sensitive to defects such as sample contamination, misfit dislocations and problems at...
the heterovalent interface. In figure 2.7a-d we show dark field and bright field images for two samples; in this macroscopic regime there should be no visible defects for samples of high quality such as the one shown in figure 2.7a,b. In figure 2.7c,d we can see a sample where misfit dislocations are present. XRR provides us with the roughness of a sample, determined quantitatively by simulating the decay slope of the oscillation signal and qualitatively by comparing that slope of different samples.

The evaluation of carrier concentration for n-type ZnₙCdₙMg_(1-y-x)Se and ZnₙCd_(1-x)Se is fairly straight forward. Samples are prepared in the van der Pauw geometry using indium contacts. After the sample is prepared the contacts are checked to be Ohmic by looking at the linearity of the standard I-V curves. Subsequently, variable field measurements are made from 0-0.5T to extract the carrier concentration and mobility. More details on how these measurements are
performed and the results from those measurements can be found later in chapter 3 (section 3.1.4.1).

2.4 MBE Growth and Characterization of the Topological Insulator Bi$_2$Se$_3$

Topological Insulators (TI) are electronic materials that have a bulk bandgap and time reversal symmetry protected conducting states at the edges or surfaces. In three-dimensional (3D) topological insulators, spin-orbit coupling is very strong and charge carrier spins are locked with momentum; this robust spin polarization is a feature that could lead to novel spintronic devices. Among 3D TIs, Bi$_2$Se$_3$ has attracted the most attention due to its relatively large bandgap (~0.3 eV) and an experimentally verified ideal Dirac cone at the Γ point in the Brillouin zone\(^9\). Angle resolved photoemission spectroscopy measurements for Bi$_2$Se$_3$ are shown in figure 2.8b\(^6\) as well as a schematic of the Dirac cone (figure 2.8c). However, a combination of its small bandgap and the low activation energy of Se vacancies has yielded material whose bulk is metallic making the

Figure 2.8: (a) Rhombohedral crystal structure of Bi$_2$Se$_3$. (b) Angle resolved photoelectron spectroscopy of the Bi$_2$Se$_3$ Dirac cone adapted from Hazzan et al\(^6\). A schematic of the spin locked Dirac cone.
measurement and use of topological surface states difficult to achieve. Several approaches have been attempted to alleviate this problem with various degrees of success, including improving the crystal quality, impurity doping with Cd and Mg and alloying with Bi$_2$Te$_3$. Heterostructures of Bi$_2$Se$_3$ with semiconductors allow us to use band engineering to realize novel properties as we demonstrate here with ZnCdSe/Bi$_2$Se$_3$ and CdTe/ Bi$_2$Se$_3$ heterostructures in chapter 6. Before any of these exiting devices can be attempted, high quality growth of Bi$_2$Se$_3$ needs to be explored.

2.4.1 Growth of Bi$_2$Se$_3$

Bi$_2$Se$_3$ has a rhombohedral crystal structure (figure 2.8a) that is made up of 5 atomic layer thick layers called “quintuple layers” (QL) that are separated by van der Waals bonded gaps typical of 2D layered materials. This weak bonding between layers coupled with very low cohesive energy between selenium and bismuth means that this material has very low surface energy. This fact allows the material to grow on many substrates and typically proceeds via the Volmer Weber (VW) growth mode. The VW growth typically manifests itself as triangular islands on the film giving it a unique surface morphology. The growth temperature for Bi$_2$Se$_3$ is similar to that of II-VI materials with a substrate temperature of 260°C found to be optimal. A BEP of Bi to Se of 1:10 has been found to give the best surface morphology at the 260°C growth temperature. Many substrates have been attempted to find the highest quality films and we will examine five different surfaces for Bi$_2$Se$_3$ epitaxy in this section.
2.4.2 Substrate Preparations

We have successfully grown Bi$_2$Se$_3$ in high quality by MBE using various substrate preparations. Among the many options, four yielded the best results (figure 2.9) and they include GaAs(111)B, InP(100) with a ZnCdSe buffer, InP(111)B with a InGaAs buffer and sapphire. Samples on III-V substrates were grown in two or three separate chambers: one where III-V substrates were prepared by first removing the native oxide and then growing the buffer; a second one in which the II-VI layer was grown, if needed; and the third for the Bi$_2$Se$_3$ growth. All the chambers were interconnected by UHV modules. For samples with a II-VI buffer first a ZnCdSe buffer was grown and then the sample was transferred via UHV transfer mechanism to a chamber dedicated to Bi$_2$Se$_3$ growth.

GaAs(111)B has the same hexagonal symmetry as the (100) hexagonal face of Bi$_2$Se$_3$. There is a lattice mismatch of 3.55% as well as many buffer options of both III-V and II-VI materials that are possible on this substrate. GaAs is also attractive because of the rich technological applications that have already been achieved on this substrate including the growth of Bi$_2$Se$_3^{64}$. Before growth of Bi$_2$Se$_3$, a 150nm thick GaAs buffer is grown on the oxide removed surface so as to smooth the surface for epitaxy. Results for layers grown on this substrate are summarized in figure 2.10. We can confirm the c-axis oriented crystal structure of the film in the XRD scan (figure 2.10b). Raman spectrum of the sample (figure 2.10c) contains four characteristic peaks,
at 37 cm\(^{-1}\), 72.5 cm\(^{-1}\), 132 cm\(^{-1}\) and 173.5 cm\(^{-1}\) corresponding to the \(E_{g1}^1\), \(A_{1g}^1\), \(E_{g2}^2\) and \(A_{2g}^2\) vibrational modes in the crystal. In AFM images, we observed (figure 2.9e) the presence of triangular features approximately 5 \(\mu\)m x 5 \(\mu\)m in area and 20 nm high. In the image in figure 2.9f we note smaller triangular features with lateral size of approximately 100 nm and a few nanometers high that grew on top of the larger features. Here, the measured RMS was approximately 2.6 nm.

Electrical measurements were conducted at \(T = 2\) K by using the van der Pauw contact configuration in magnetic fields up to 5 T applied in the direction perpendicular to the film’s plane. Figure 2.10d shows a cusp in the magnetoresistance (MR) measurement consistent with weak anti-localization for Bi\(_2\)Se\(_3\). We can fit the conductance data to 2D transport theory\(^{65}\) and the fit extracted which is consistent with the presence of surface states. From the Hall measurements, our sample was found to be n-type. The sheet carrier concentration was

![Image](image_url)

Figure 2.10: (a) Schematic of Bi\(_2\)Se\(_3\) sample grown on GaAs(111)B sample grown and characterized. (b) \(2\theta-\omega\) x-ray diffraction scan showing the diffraction peaks from GaAs(111)B and Bi\(_2\)Se\(_3\). (c) Raman spectra from Bi\(_2\)Se\(_3\) showing the modes in the sample. (d) Magneto-resistance measured at 2K in the Van der Pauw configuration showing the weak anti-localization signature of Bi\(_2\)Se\(_3\). (e,f) Atomic force micrographs of the sample with showing the morphology of the film. The RMS roughness of the film is ~2.6 nm.
approximately $4 \times 10^{13}$ cm$^{-2}$ and the mobility was $520$ cm$^2$(Vs)$^{-1}$ comparable with that of samples grown on GaAs by other groups$^{64}$. Of the III-V substrates InP (111) is particularly attractive due to its very close lattice matching to Bi$_2$Se$_3$.

The next surface we analyzed was InP(111)B with an InGaAs buffer. This surface is particularly appealing because of its strong chemical interaction, low lattice mismatch (0.2%) and symmetry with Bi$_2$Se$_3$. Sharp and streaky (1x1x1) patterns were observed for these samples. In XRD we noted peaks for InP(111) and the peaks for c-axis oriented Bi$_2$Se$_3$ (figure 2.11b). AFM
micrographs showed the best results of any substrate attempted with RMS roughness of ~0.3nm. Transport measurements showed similar results as those presented for InP(100).

In order to improve the chemical compatibility of the InP(100) substrate, a ZnCdSe buffer was used to grow Bi2Se3. The (100) surface was chosen because the quality of grown ZnCdSe is much better than that on InP(111)B and it has a smaller mismatch to Bi2Se3 than GaAs(111)B with ZnSe used by other groups64. The results for this sample are summarized in figure 2.12 and the structure of the sample is shown in figure 2.12a. In figure 2.12a we see (2x1) reconstruction of the selenium rich InP lattice matched ZnCdSe surface. When beginning to grow Bi2Se3 we see a transformation of the RHEED pattern to a 1x1x1 Bi2Se3 surface (figure 2.12b) with the
presented streaks repeating every $60^\circ$ indicating its hexagonal structure. In XRD of the sample (figure 2.12d) we can see the diffraction peaks from ZnCdSe, InP and Bi$_2$Se$_3$. In Raman studies (figure 2.12e) we again observe the corresponding peaks for the crystal symmetry from group theory. To confirm the epitaxial growth of Bi$_2$Se$_3$, HRTEM studies were performed (figure 2.12f) and we noted a smooth interface between the buffer and the grown layer with very good crystalline quality. AFM studies of the sample (figure 2.12g) showed RMS of $\sim 0.8\text{nm}$. MR data shows that the film is n-type and carrier concentrations of $7\times10^{12}$ with mobilities of $700\text{cm}^2(\text{Vs})^{-1}$ are comparable to the best reported results for MBE grown Bi$_2$Se$_3$ samples on any substrate.

The last substrate we attempted was sapphire. This substrate was chosen because it is very insulating and therefore does not modify the transport results. Despite the very large lattice mismatch, the weak chemical interaction allows high quality Bi$_2$Se$_3$ to be grown if nucleation can be achieved. Nucleating can begin by growing a low temperature Bi$_2$Se$_3$ buffer grown at $110^\circ\text{C}$. The results for this substrate were like InP in terms of RMS of $\sim 0.6\text{ nm}$ and similar results are seen in XRD, RHEED and transport measurements.

2.4.3 Twin Suppression in Bi$_2$Se$_3$

It is important to note that one common defect observed in these samples is the presence of triangular features due to the VW growth mode of Bi$_2$Se$_3$. These triangular features can be oriented in two different directions according to symmetry of stacking in each region (figure 2.8a). These two regions are known as twins and when two twins come together a dislocation defect is formed at their interface. Twinning is one of the most common defects in hexagonal films since there is a low energy symmetry operation between the two phases. In figure 2.13 we
show the morphology of Bi$_2$Se$_3$ films with (figure 2.13a) twin domains and with twin domain suppression (figure 2.13b). There are several ways to suppress twin domains common in hexagonal materials. Those include reducing the symmetry of the substrate; this was done for all samples in this section by using 0.2° offcut sapphire substrates. As we shall see, this method is not effective for Bi$_2$Se$_3$ on sapphire because of the low binding energy to the substrate. Another way is to modify the energetics of nucleation to favor one symmetry over the other. This is achieved by carefully prepared buffer sequences and is the focus of this section of the chapter. The sequences attempted are summarized in table 2.1. These steps include no modification of the growth sequence (sample 1); a growth and subsequent removal of Bi$_2$Se$_3$ by heating the substrate to 340°C and then regrowth of the layer (sample 2, 3 and 4); an additional 4 minute annealing step after the second growth of Bi$_2$Se$_3$ (sample 3); and bismuth exposure before any growth occurs (sample 4).
Figure 2.14: (a) X-ray diffraction scan of the (006) reflection of Bi$_2$Se$_3$ showing clearly defined thickness fringes from which the thickness is extracted. (b) Double crystal rocking curves of the four samples

Table 2.1 Buffer sequences for twin suppression on Bi$_2$Se$_3$ on sapphire:

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Preparation</td>
<td>1 min @ 140°C</td>
<td>1 min @ 140°C</td>
<td>1 min @ 140°C</td>
<td>Bi only for 1.5 min</td>
</tr>
<tr>
<td></td>
<td>4 min @ 275°C</td>
<td>4 min @ 275°C</td>
<td>4 min @ 275°C</td>
<td>1 min @ 140°C</td>
</tr>
<tr>
<td></td>
<td>Remove layer</td>
<td>Remove layer</td>
<td>Remove layer</td>
<td>4 min @ 275°C</td>
</tr>
<tr>
<td></td>
<td>1 min @ 140°C</td>
<td>1 min @ 140°C</td>
<td>1 min @ 140°C</td>
<td>1 min @ 140°C</td>
</tr>
<tr>
<td>Buffer Annealing</td>
<td>None</td>
<td>None</td>
<td>4 min @ 275°C</td>
<td>4 min @ 275°C</td>
</tr>
<tr>
<td>Growth</td>
<td>2h @ 270°C</td>
<td>2h @ 275°C</td>
<td>2h @ 275°C</td>
<td>2h @ 275°C</td>
</tr>
</tbody>
</table>

XRD results for these samples is summarized in figure 2.13. XRD 2θ-ω scans, like the one shown for sample 1 (figure 2.14a), were used to extract the thickness. In these scans, clearly defined Pendellösung fringes are indicative of high quality material and reveal a thickness of 46nm, 37nm, 38nm and 37nm for samples 1, 2, 3 and 4 respectively. In figure 2.14b rocking curves for all four samples are presented showing similar linewidths of ~300 arcsec consistent with the best reported values in the literature. XRD ϕ scans of the (1015) asymmetric reflection show magnitude of twin suppression for all four samples. The amount of suppression can be quantified by the ratio of the intensity of one phase over the other. The extracted twin ratios for these samples was 1.1, 3.1, 6.0 and 9.8 for samples 1, 2, 3 and 4 respectively. This result demonstrates that significant twin suppression can be achieved on sapphire substrates by
Figure 2.15: $\phi$-ω maps of sample 1 and 3 used to extract the orientation of twin domains.

modification of the nucleation steps with the best results for sample 4 with bismuth exposure before growth.

To explore the texture of the twin domains $\phi$-ω, maps were performed for samples 1 and 3 (figure 2.15). With these scans, we can determine the presence of any additional phases that might exist in the film and can see that only two twin phases are present shown by two overlaid oscillations in the scan. We can also extract the tilt between the twin phases to further understand the nature of the twin domains in each sample. We extract from these scans a tilt between the two twins of $0.38^\circ$ for sample 1, and a tilt of $0.06^\circ$ for sample 3. This finding is important because in addition to suppressing the twins in the samples, the two phases are much more aligned with the growth modifications, and twinning may be completely removed with further experimentation.
In this chapter, we have demonstrated that high quality bulk material can be achieved by careful control of the parameters of growth. Once bulk material is grown and found to be of high quality for both InP based II-VI materials and Bi$_2$Se$_3$, we can begin to incorporate them into heterostructures as will be executed throughout the remainder of this dissertation.
3 Material Optimization for II-VI Quantum Cascade Emitters:

Improved doping strategy, reduced lattice mismatch and growth interruptions

3.1 5µm Quantum Cascade Emitters

3.1.1 Summary

Quantum Cascade emitters are highly engineered quantum structures that require extreme control of interface quality, doping profiles and low defect densities. We report on investigations of the doping, lattice-mismatch and interface quality for the molecular beam epitaxial growth of ZnCdSe/ZnCdMgSe/InP quantum cascade emitter structures with improved electrical, structural and spectral properties. An improved doping strategy, the control of the lattice mismatch to less than 0.25% and the incorporation of growth interruptions have led to quantum cascade structures with good I-V characteristics and electroluminescence emission up to room temperature, with an emission energy of 230 meV (5.4 µm) and a full-width at half maximum of 41 meV at 80K, significantly improved over earlier attempts without these refinements. These are the best device properties reported so far for this material system, and are the best reported from any non-III-V material. It is expected that the addition of waveguide layers in the structure will lead to the observation of lasing.

3.1.2 Introduction

In this section, we present the growth and characterization of ZnCdSe/ZnCdMgSe quantum cascade(QC) heterostructures grown via molecular beam epitaxy(MBE) and designed to operate
at ~5µm. Semiconductor lasers operating in the first infrared transmission window (3-5µm) have many possible scientific, medical, environmental, industrial and military applications. Important applications include high-resolution chemical spectroscopy, process monitoring, pollution monitoring and countermeasures. Shorter wavelength coherent infrared sources are of interest in high-resolution spectroscopy and trace gas-sensing applications. Since they were first demonstrated in 1994\textsuperscript{32}, QC lasers have had great success using the AlInAs/InGaAs/InP material system. The successes of these QC lasers include continuous-wave room temperature operation\textsuperscript{66}, wall plug efficiencies as high as 40-50\%\textsuperscript{67} and watt level emission in the 3.7-5 µm range\textsuperscript{68,69}. Due to a limiting conduction band offset (CBO) of 0.72 eV, it is difficult to obtain a good performance at the shorter wavelengths with those materials. To overcome the CBO limits there has been significant research into exploring other materials for QC laser applications.

New materials being investigated include InAs/AlSb on InAs\textsuperscript{70}; InGaAs/AlAsSb on InP\textsuperscript{71}; InAlAs/AlAs on InP\textsuperscript{72}; AlN/GaN\textsuperscript{73}; and ZnCdSe/ZnCdMgSe on InP\textsuperscript{74}. Although the InAs/AlSb system has the advantage of a CBO of up to 2.1 eV, and has to date achieved the lowest QC lasing wavelength of 2.6 µm\textsuperscript{70}, intervalley scattering reduces the effective CBO, limiting the achievable emission any further. Success has also been obtained in the InGaAs/AlAsSb material system, with devices yielding optical powers greater than 3.5 W in the 3.3-3.5 µm range\textsuperscript{71}. Lasing has been observed in the InAlAs/AlAs system with wavelengths as short as 3.05 µm at 80K\textsuperscript{72} but shorter wavelengths are not expected due to its limited CBO. Intersubband detectors have been reported from AlN/GaN materials but QC electroluminescence has been elusive to date\textsuperscript{73}. 
The ZnCdSe/ZnCdMgSe material system is also an attractive alternative\textsuperscript{74}. ZnCdSe/ZnCdMgSe has a direct bandgap, no intervalley scattering and a CBO as high as 1.12\,eV; this makes it a good candidate for devices operating in the 3-5 \,\mu m range\textsuperscript{75,76} and possibly at wavelengths as low as 1.55 \,\mu m. We have previously reported electroluminescence in this material system in the 4 to 5 \,\mu m range\textsuperscript{76,77}. However, lasing from these structures has not yet been observed, likely due to non-optimized materials. In particular, QC laser structures with high Mg content ZnCdMgSe waveguide layers, which are needed for effective wave guiding, exhibit high resistivity\textsuperscript{77} and the QC laser structures often develop crystalline defects during the MBE growth\textsuperscript{78}. Furthermore, the alloy nature of the two constituent materials may result in non-abrupt interfaces, which may affect electron tunneling. Here, we address these concerns by 1) calibration of the ZnCl$_2$ doping for the very wide bandgap (E$_g$ $>$ 2.9 \,eV) ZnCdMgSe layers used in the structures and optimization of the laser doping technique; 2) a more detailed examination of the effect of lattice mismatch on the deterioration of the materials during growth and a determination of the mismatch tolerance of the structures; and 3) the incorporation of growth interruptions during the growth of the active core of the QC laser to improve the interface quality of the multi-layers. Although emission at $\sim$3\,\mu m is our goal, our current priority is to demonstrate lasing, so our structures are designed for the less demanding 4-5 \,\mu m wavelength range.

### 3.1.3 Experimental

#### 3.1.3.1 Heterostructure Growth

The samples were grown by MBE on (001) S doped InP substrates. A dual chamber Riber 2300P system equipped with \textit{in-situ} reflection high-energy electron diffraction (RHEED) was used. The samples were grown by first deoxidizing the surface of epi-ready InP (001) in a chamber
dedicated to the growth of III-V materials. Following the removal of the native oxide, an InGaAs layer doped with Si (n~8x10^{18} cm^{-3}) was grown with a thickness of ~250 nm at a nominal temperature of 500°C. The samples were cooled to room temperature and then transferred via ultra-high vacuum transfer modules to a chamber dedicated to the growth of II-VI materials where the substrate temperature was raised to 165°C. There the surface was exposed to a Zn flux for 40 seconds, followed by the growth of a ZnCdSe 10 nm thick buffer layer at 165°C. The substrate temperature was subsequently raised to 270°C and the rest of the structure was grown under Se stabilized growth conditions. All layers are grown closely lattice matched to the InP substrate. For the doping calibrations, single layers of ZnCdMgSe and ZnCdSe were grown using various ZnCl₂ cell temperatures. The quaternary ZnCdMgSe layers were always capped with a thin (~12 nm) ZnCdSe layer to avoid oxidation. The various multi-layer structures investigated are summarized in figure 1. For electrical characterization two different QC laser structures with waveguide layers were grown (figure 3.1a,b). In these, two different types of waveguide layers were investigated: thick ZnCdMgSe barrier layers with a 77K bandgap of 2.95 eV in the structure designated as QC1, and thinner ZnCdMgSe barrier layers with a somewhat lower 77K bandgap of 2.8 eV in the structure designated as QC2. All samples in this section utilize ZnCdSe (Eg~2.08) closely lattice matched to InP. The design of the active core, which includes injectors and active regions, were the same in both structures. The layer sequence in angstroms beginning with the injector of one period of the active region of QC1 (repeated 50 times) and QC2 (repeated 40 times) is as follows: 15/20/15/18/15/15/14/16/12/18/11/10/25/10/23/13/21 with the ZnCdMgSe barriers designated in boldface and Cl-doped (n~3x10^{17} cm^{-3}) layers underlined. For the core region, ZnCdMgSe layers with Eg = 2.95eV (at 77K) were employed. Several additional QC laser structures similar
in design to QC1 and QC2 were considered in the investigation as to the effect of lattice mismatch on material quality. To examine the effect of growth interruptions four separate samples were grown. Two multiple quantum well (MQW) samples designated MQW 1 and MQW 2 (figure 1d) were grown consisting of single ZnCdSe QWs (20 Å) separated by ZnCdMgSe barriers (110 Å), repeated 20 times. In addition, two QC structures without waveguide layers were grown designated as EL1 and EL2 (figure 3.1c). The layer sequence in angstroms for one period of EL1 and EL2 (figure 3.1c). The layer sequence in angstroms for one period of EL1 and EL2 beginning with the injector is as follows: 10/20/10/18/12/17/14/16/15/20/36/8/30/9/26 with the ZnCdMgSe barriers designated in...
boldface and Cl-doped (n~3\times10^{17} \text{ cm}^{-3}) layers underlined (repeated 40 times). The ZnCdMgSe bandgap in these structures was 3.0 eV. MQW1 and EL 1 and were grown with no growth interruptions between layers, while MQW2 and EL2 were grown by closing the shutters for 20 seconds at all the interfaces between the barriers and wells in the structures. The Selenium shutter was left open during the growth interruptions.

3.1.3.2 Characterization

In addition to the in-situ RHEED measurements made during the growth of the III-V buffer layer and the II-VI layer structures, post growth characterization of the materials was performed. High-resolution x-ray diffraction (HR-XRD) measurements were made with a Bruker D8 Discover with da Vinci design. Photoluminescence (PL) measurements were made with an Omnichrome He-Cd laser at a wavelength of 325 nm with a power rating of ~30 mW. To observe the PL emission from the active core of the QC and EL structures, the samples were etched with a 1% bromine-methanol solution to remove the top ZnCdSe layer prior to the measurement. PL measurements for MQW1 and MQW2 were taken without etching. Hall measurements were made with indium contacts using the van der Pauw configuration. I-V and electroluminescence measurements were made by etching a lithographically patterned 200 µm mesa with a HBr:HNO_3:H_2O (1:1:10) wet chemical etch solution. A second lithography step was incorporated to evaporate Ti/Au (250Å/3000Å) top and bottom contacts. An O_2 plasma cleaning followed by HF:H_2O (1:1) was utilized immediately before contact deposition. Mesas were then cleaved into semicircular structures and electrical contacts where wire bonded to contact pads.
3.1.4 Results and Discussion

3.1.4.1 Electrical Properties

The results of the doping calibration of the wide bandgap ZnCdMgSe layers are summarized in figure 3.2, where the carrier concentration and mobility of the ZnCdSe:Cl (green circles) and ZnCdMgSe:Cl alloys (red squares) are plotted against the inverse of the dopant cell temperature. Previously published results in ZnCdSe are shown for comparison (grey triangles). From this data we observe that our ZnCdSe layers exhibited a dopant incorporation behavior and a maximum doping level of \( n \sim 3 \times 10^{18} \text{ cm}^{-3} \) obtained with a nominal ZnCl\(_2\) cell temperature of \( \sim 77^\circ\text{C} \), similar to those previously reported\(^{50}\). A sharp decrease in carrier concentration as the ZnCl\(_2\) temperature is increased beyond the maximum doping level suggests the presence of compensation possibly from the formation of defects in the material as the Cl concentration exceeds an optimum value. Comparable mobilities with those previously reported are also observed in the ZnCdSe samples. Previous reports of n-type doping of ZnCdMgSe\(^{50}\) layers with bandgaps of 2.74 eV gave a maximum doping level of \( n \sim 3 \times 10^{18} \text{ cm}^{-3} \). The n-type doping of the ZnCdMgSe:Cl with larger bandgaps (\( E_g \sim 2.95 \text{ eV at 77K} \)) measured here exhibited significant scatter due to the inherent difficulties in measuring these materials because of their low mobilities. The highest doping level obtained was \( n \sim 8 \times 10^{17} \text{ cm}^{-3} \) with a nominal ZnCl\(_2\) cell temperature of 62\(^\circ\text{C}\). Several samples grown at ZnCl\(_2\) cell temperatures higher than 68\(^\circ\text{C}\) were grown but could not be measured. Thus, we conclude that compensation occurs at a much lower ZnCl\(_2\) cell temperature for this ZnCdMgSe material in comparison to ZnCdSe. Although the maximum doping level for the 2.95 eV bandgap quaternary materials is low, it does not preclude
the fabrication of QC lasers, but it is important to note that too high a ZnCl₂ cell temperature can render the material insulating, and prevent the possibility of lasing.

To avoid the formation of highly resistive material we must insure that the dopant cell temperature is always below the temperature associated with high resistivity. Figure 3.3a shows the I-V characteristics of QC1 and QC2 grown using these doping strategies. Good electrical
properties can be seen, such as low turn on voltages and low resistivity after turn-on in both samples. Reducing the bandgap of the waveguide layer, as was done in QC2, results in slightly better electrical properties, for example a turn on voltage of 9.5V for QC2 compared to 14V for QC, measured at 80K (not shown).

3.1.4.2 Crystal Quality

We have already reported that the substrate temperature and lattice mismatch play a significant role in the crystal quality of QC laser structures grown with II-VI materials\textsuperscript{78}. However, even after efforts to take those observations into account, the yields of good QC laser structures have remained low. To address the low yields we have investigated further the effect of lattice mismatch in order to establish the maximum mismatch that can be tolerated in the growth of these structures before the materials degrade. We have also explored the effect of incorporating growth interruptions between layers during growth. This incorporation has been shown in other materials to improve the interfaces between two alloys, and to reduce the propagation of defects through the structure\textsuperscript{79}.

Figure 3.3 (a) I-V measurements of sample QC1, and QC2 at 300 K. (b) I-V measurements for EL1 (grown with interruptions) and EL2 (grown without interruptions) at 300K.
Our earlier investigations into the mechanisms of the appearance of spots in the RHEED pattern during growth of some of our samples (illustrated in the inset of figure 3.4) suggest the formation of rock salt domains within our structures\textsuperscript{78}. There we proposed that misfit dislocations due to lattice mismatch were one of the defects that could induce the formation of these undesirable rock salt domains. Samples that exhibit these RHEED spots have never shown good device performance. To further quantify the mismatch tolerance in our samples, we have analyzed the data obtained during the growth of several QC samples with thick waveguides. The result of that
Chapter 3: Growth Interruptions in II-VI QC Emitters

Figure 3.5: High resolution x-ray diffraction for the (004) reflection in multiple quantum well structures with and without growth interruptions.

analysis, presented in figure 3.4, plots the time that it takes for the RHEED spots to appear (or the onset of the spots) as a function of the lattice mismatch of the structure. Since the structures contain several layers, the mismatch of the layer with the maximum lattice-mismatch was plotted. The data shows a clear correlation between the two variables, with the spots appearing much sooner when the lattice-mismatch is large. A dashed line was drawn to aid the eye and to illustrate the relationship. Furthermore, when the lattice mismatch is less than 0.25% the spots did not appear within the time that it takes to grow the full structure (~400 minutes) for two of the three samples studied. If we extrapolate the dashed line from the samples with larger mismatch we can project the time when the spots would appear in those samples (shown in the figure 3.4 as open triangles). Thus, we conclude that if the lattice mismatch does not exceed 0.25%, the full structure is likely to grow without the appearance of RHEED spots. As can also be seen from the graph, one sample (green triangle) exhibited RHEED spots despite having a low
lattice mismatch suggesting that other defects in the material besides misfit dislocations, such as perhaps stacking faults, may also lead to the appearance of these spots.

Growth interruptions at the heterointerfaces are expected to improve the interface quality of the materials. In order to probe the effect of using growth interruptions between the alternating layers in these structures, we grew two test samples (MQW1 and MQW2). HR-XRD scans of the (004) reflection for those two samples are shown in figure 3.5. The sample that was grown with interruptions (MQW2) has more well-defined thickness fringes indicative of better overall sample quality, and sharper and more well-defined superlattice peaks, indicative of more abrupt interfaces.

Figure 3.6: 77K photoluminescence spectra for samples MQW1 (without growth interruptions) and MQW2 (with growth interruptions).
The 77K photoluminescence (PL) measurements for these two samples, shown in figure 3.6, reveal slightly narrower peaks for MQW2, grown with growth interruptions: a FWHM of the excitonic peak of 45.1 meV (\(\Delta E/E=0.0180\)) for MQW1 compared to a FWHM from the excitonic peak of 41.5 meV (\(\Delta E/E=0.0170\)) for MQW2. Narrower PL linewidths are also consistent with more abrupt and better quality interfaces.

### 3.1.4.3 Devices

To evaluate the impact of incorporating all these findings into a device structure, we proceeded to grow two QC structures without waveguide layers, designated as EL1 and EL2. The two constituent alloy compositions were carefully calibrated to maintain a lattice mismatch of less than 0.25%. The dopant cell temperatures for the ZnCdSe and ZnCdMgSe were kept at a nominal 60ºC and 62ºC, respectively, below the maximum temperature before compensation. Lastly, to test the effect of the growth interruptions on the device properties, one sample (EL2) was grown with growth interruptions and the other (EL1) without growth interruptions during the growth of the core active region.
The HR-XRD results for the (004) and the (002) reflections for EL1 and EL2 can be seen in figures 3.7a and 3.7b. No significant change in the (004) XRD data is observed; both scans are representative of very good material quality. However, a slight improvement in the superlattice peak widths can be seen in the (002) HR-XRD scan for EL2.

The 77K PL measurements for EL1 and EL2 are shown in figure 3.8. A narrower PL peak was observed for the sample with interruptions (EL2), with a FWHM from the excitonic peak of 30.8 meV corresponding to a $\Delta E/E$ value of 0.136 compared to a FWHM from the excitonic peak of 36.6 meV corresponding to a $\Delta E/E$ of 0.156, for the sample without interruptions (EL1).

Devices were fabricated from EL1 and EL2 and their I-V characteristics and electroluminescence emission spectra were measured. The I-V data for EL1 and EL2, presented in figure 3(b), shows
low turn-on voltages and low resistivity, like those in QC1 and QC2. Also, there is no significant
difference between the I-V characteristics of EL1 and EL2, suggesting that no deleterious effects
are produced by the addition of growth interruptions. Electroluminescence spectra at 80K were
measured at several currents and are shown in figure 3.9. The results show a dramatic difference
between the two samples. The FWHM of the electroluminescence of EL1 (figure 3.9a), grown
without interruptions, was 641 cm\(^{-1}\), comparable to the value of 575 cm\(^{-1}\) previously reported\(^{12}\) in
a similar structure, while in EL2 (figure 3.9b), which was grown with growth interruptions, the
electroluminescence FWHM was 358 cm\(^{-1}\), corresponding to a 45% reduction in linewidth.
Furthermore, the electroluminescence efficiency, as indicated by the peak intensity at a particular
driving current, is increased by more than 2-fold in EL2 compared to EL1. Finally, room
temperature electroluminescence (not shown) was only observed for sample EL2. These EL
emission linewidths and efficiencies obtained for EL2 are the best reported so far for
ZnCdMgSe-based QC structures grown without waveguide layers.

Figure 3.9: Electroluminescence spectra at 80K using different injection current densities for
samples (a) EL1 (without growth interruptions) and (b) EL2 (with growth interruptions).
3.1.5 Conclusions

In order to improve the quality and yield of QC laser structures made from ZnCdSe/ZnCdMgSe heterostructures grown on InP substrates we have: 1) investigated the n-type doping of ZnCdMgSe layers with wide bandgaps ($E_g \sim 2.95$ eV) and established a doping strategy to achieve low resistivity in these wide bandgap materials; 2) determined the tolerance of lattice mismatch that can be accommodated in QC laser structures before the materials degrade through the formation of RHEED spots; 3) improved the interface quality of the multilayers by the incorporation of growth interruptions at the ZnCdSe/ZnCdMgSe interfaces. We concluded that to obtain good I-V characteristics, the doping of the constituent alloy layers must be well calibrated and the dopant cell temperature used during growth tailored to the alloy composition being grown to avoid compensation, especially when very wide bandgap layers are utilized for this device structure. We also determined that the material quality (as evidenced by the appearance of RHEED spots during growth) can be significantly improved when lattice mismatch is not allowed to exceed 0.25% for structures with thick waveguides. Finally, we have found that the spectral properties of the QC electroluminescent devices can be greatly improved by implementing growth interruptions during the growth of the active core of the device structure. Applying a combination of the above three findings, QC structures with excellent I-V and electroluminescence properties were grown. We anticipate that the electroluminescent properties of QC structures will be further enhanced by including appropriate waveguide layers and that the resulting devices should exhibit efficient lasing.
Chapter 3: Growth Interruptions in II-VI QC Emitters

3.2 6-8µm Quantum Cascade Emitters

3.2.1 Summary

Now we turn our attention to the MBE growth and characterization of ZnCdSe/ZnCdMgSe quantum cascade(QC) heterostructures designed to operate at 6-8µm. These structures utilize the better-understood ZnCdMgSe with InP lattice matched compositions yielding a bandgap of 2.80 eV as compared to previous work which used ZnCdMgSe compositions with bandgaps at 3.00 eV. Grown structures possess good structural and optical properties evidenced in x-ray diffraction and photoluminescence studies. Fabricated mesa devices show temperature dependent I-V measurements with a differential resistance of 3.6 Ω, and a turn on voltage of 11V consistent with design specifications. Electroluminescence was observed in these devices up to room temperature with emission centered at 7.1 µm and line widths of ~16%(ΔE/E) at 80K. The results show that these are well-behaved electroluminescent structures. The addition of waveguide layers and further improvements in well barrier interfaces are being pursued in efforts to demonstrate lasing.

3.2.2 Introduction

Despite improved performance from the structures presented above, lasing from structures made from this system has not yet been observed, likely due to non-optimized materials properties. To understand and possibly overcome the absence of lasing we propose to design and grow devices that operate in the 6-8 µm range. This wavelength range relaxes the design requirements and allows for the use of a 2.80 eV bandgap ZnCdMgSe barrier layer, which has a lower Mg content than the previously used composition with a 3.00 eV bandgap. This new composition has well-studied material parameters and is easier to grow in high quality\textsuperscript{48}. The simplified design
specification, presented in figure 1, which also includes shorter injector regions and thus fewer layers, generally allows for the study of problems related to performance present in the more technologically challenging short wavelength devices. This path mirrors the development of QC devices in III-V materials in the early stages of development. In this research, we explore the molecular beam epitaxy (MBE) growth and characterization of a structure designed for emission centered at 6.5µm. This structure incorporates a three-well, bound-to-bound active region and short injector design as a first step in the demonstration of long wavelength II-VI based QC laser devices.

3.2.3 Experimental

3.2.3.1 MBE Growth

The growth procedure for the long wavelength devices is the same as that for the short wavelength devices discussed in the previous section. The only significant difference is that a Zn$_{0.33}$Cd$_{0.3}$Mg$_{0.37}$Se quaternary was used with significantly lower Mg content to achieve higher quality material.

3.2.3.2 Device Design

The design layer sequence in angstroms of one period of the active-injector region, beginning with the thickest well and repeated 40 times, is as follows: 42/10/34/10/26/10/21/12/15/12/14/12 with the ZnCdSe well layers designated in boldface and Cl-doped (n~3x10$^{17}$ cm$^{-3}$) layers underlined. The conduction band profile for two repeats of an active-injector region is shown in figure 3.10. For the core region, Zn$_{0.33}$Cd$_{0.3}$Mg$_{0.37}$Se layers with $E_g$=2.83eV were employed. At the interface between barriers and wells, 20s growth interruptions with a Se overpressure were incorporated into the growth sequence to improve the interface quality. The complete sample
design beginning at the bottom of the structure is as follows: 300 nm In$_{0.53}$Ga$_{0.47}$As buffer; 10nm Zn$_{0.5}$Cd$_{0.5}$Se buffer; a 400 nm Zn$_{0.5}$Cd$_{0.5}$Se:Cl (n~3x10$^{17}$); the active core described above; 200 nm Zn$_{0.5}$Cd$_{0.5}$Se:Cl (n~3x10$^{17}$) layer; and a 200 nm Zn$_{0.5}$Cd$_{0.5}$Se:Cl highly doped (n~1x10$^{18}$) contact layer.

3.2.3.3 Characterization

High-resolution x-ray diffraction (HR-XRD) measurements were made with a Bruker D8 Discover with da Vinci design. Photoluminescence (PL) measurements were made with an Omnichrome He-Cd laser at a wavelength of 325 nm using a HR4000 Ocean Optics spectrometer. To observe the PL emission from the active core, samples were etched with a 1% bromine-methanol solution to remove the upper layers prior to the measurement. Electroluminescence measurements were performed utilizing a Thermo-fisher 8700 Fourier transform infrared (FTIR) spectrometer in step scan mode with a lock-in amplifier. All presented electroluminescence spectra are taken with a ZnSe polarizer set to transverse magnetic (TM), and then repeated at 90°, transverse electric (TE), to verify intersubband (ISB) origin. A liquid

![Figure 3.10: Band diagram of active core design used in device.](image-url)
nitrogen cooled mercury cadmium telluride detector was used to measure the emitted light. Devices were fabricated into 250µm half circular cleaved mesas by optical lithography and wet etching.

3.2.4 Results and Discussion

3.2.4.1 X-ray Diffraction

High resolution x-diffraction (HR-XRD) measurements of the sample are presented in

Figure 3.11: (A) High resolution x-ray (002) scan of sample showing sharp and strong superlattice fringes and a full width at half maximum polynomial fit of the zero order superlattice peak of 95 arc seconds (inset). (B) High resolution x-scan (004) showing the mismatch of the various layers in the heterostructure. (C) X-ray reflectance (XRR) scan of the structure showing a period of 24.7 nm and good interface quality.
Chapter 3: Growth Interruptions in II-VI QC Emitters

Figure 3.11a. This measurement shows strong and sharp satellite peaks consistent with the high quality of the structure grown. In these measurements, we observed full width at half maximum (FWHM) of 95 arc seconds for the zero order superlattice as calculated from a polynomial fit to superlattice fringes. The identity of the In$_{0.53}$Ga$_{0.47}$As peak was determined utilizing a calibration sample grown the same day with the same growth conditions (not shown). Once the zeroth order SL peak was identified, the remaining peak was assigned to the Zn$_{0.5}$Cd$_{0.5}$Se layers. This assignment was in agreement with the energy dependence of PL measurements. HR-XRD (004) measurements show the lattice mismatch of -0.15% for Zn$_{0.5}$Cd$_{0.5}$Se, 0.02% for In$_{0.53}$Ga$_{0.47}$As, and 0.09% for the active core. Close lattice matching to the InP substrate is necessary to prevent misfit dislocations. X-ray reflectance (XRR) studies on the sample (figure 3.11c) give a period of 24.7 nm. The discrepancy between the design and measured period is due to a somewhat faster growth rate than calibrated and a shutter error in the growth of the 42Å well, making it ~54Å thick. This error also led to a shift in the operating bias and wavelength of the device. XRR measurements show good interface quality for II-VI materials in the active core and throughout the structure.

3.2.4.2 Photoluminescence

Photoluminescence measurements (figure 3.12) show the optical characteristics of the structure as one traverses along the growth direction by the use of etching to reveal the lower lying layers. Strong sharp PL emission is observed in each region of the sample originating from the different layers in the structure, consistent with high quality material. We only observe a weak deep level emission in the sample etched for the longest time, suggesting that it originates from defects near the heterovalent interface. The FWHM of the bottom Zn$_{0.5}$Cd$_{0.5}$Se layer is 24 meV and 31 meV for the top Zn$_{0.5}$Cd$_{0.5}$Se layer. Both top and bottom Zn$_{0.5}$Cd$_{0.5}$Se layers have a bandgap near 2.16
eV at 77K. The active core has a bandgap near 2.24 eV at 77K and a FWHM of 24 meV. A FWHM of 24 meV for the active core shows the material to be of high quality, similar to that of single quantum wells in high quality materials, and indicates uniformity in thickness of the quantum wells across the structure. The linewidths for the top and bottom Zn$_{0.5}$Cd$_{0.5}$Se bulk layers are consistent with our best II-VI material quality measured at 77K.

3.2.4.3 Device Performance

Pulsed I-V measurements of fabricated mesa devices done at 5 kHz (100 ns pulse width) are presented in figure 3.13a. We observe low differential resistance (3.2 Ω at 300K) indicative of very good electrical properties, comparable with III-V devices of similar design. Measured turn on voltage of 11 V is consistent with the design.
Electroluminescence (TM) measurements performed at 80 kHz (200 ns pulse width) as a function of current (figure 3.13b) and temperature (figure 3.13c) show a Gaussian line-shape with a peak centered at \( \sim 7.1 \mu m \) up to 160 K. Linewidths of \( \sim 16\% (\Delta E/E) \) at 80 K are observed, which are
somewhat wider than those typically seen on III-V materials. The peak at 7.1µm goes to zero when the polarizer is rotated 90˚ verifying its ISB origin. At about 180K a second peak is observed that is not polarization dependent suggesting it is of thermal origin. This peak dominates the spectra at higher currents, so spectra taken at 1A are presented above 180K. A better understanding of the origin of this peak is being pursued. Emission from the 7.1µm peak persists up to 280K. The presence of ISB electroluminescence up to room temperature will enable us to investigate further the optimization of the QC laser structure with these materials.

3.2.5 Conclusions

We have shown the detailed material properties and electroluminescence characteristics of the first reported II-VI long-wave (7.1µm) QC emitter. The QC design was optimized and made robust by using a lower bandgap ZnCdMgSe quaternary barrier layer as well as short-injector regions. MBE growth of a high-quality structure was carried out and observed to exhibit excellent II-VI crystal quality both optically and structurally. Fabricated devices showed best-reported I-V characteristics for II-VI materials QC structures, with the expected turn on voltage and low differential resistance. Electroluminescence at 7.1 µm was observed up to 280 K. The results suggest that these structures are good candidates to pursue lasing from these materials. Future work involves design and growth of full devices, with waveguide ZnCdMgSe/ZnCdSe layers, which are expected to lead to the demonstration of lasing from these materials.
4 Device Applications of II-VI Materials with Improved Interfaces

In this chapter, we examine a series of devices that have been pursued made from the ZnCdMgSe based materials that have been discussed and optimized utilizing the growth techniques and procedures outlined previously. These devices include optically pumped II-VI “green gap” disk lasers and quantum cascade detectors (QCDs). In both applications, the unique properties of these materials along with the high quality that has been achieved via the growth optimization schemes described above have enabled us to demonstrate state of the art device characteristics that are not available with currently used materials for these devices.

4.1 Quantum Cascade Detectors

This section focuses on the development of quantum cascade detectors (QCD) made from II-VI materials, and includes the first demonstration of a II-VI QCD in the literature. The initial realization of a broadband QCD spanning a large range of the IR spectrum is also presented. Additionally, the first display of a hybrid II-VI/III-V device in a monolithic hybrid QCD is shown. These devices represent a significant technological validation of the capabilities and potential of InP based II-VI materials.

The need for high performance room temperature infrared (IR) detectors has important applications in spectroscopy, medical, industrial and defense applications. High performance emitters and detectors in this technologically important range have been the focus of scientists and engineers for several years. However, band to band detectors such as mercury cadmium telluride (MCT) and InSb have kept their operation at or near liquid nitrogen temperatures. Therefore, III-V intersubband (ISB) devices have been of intense interest in the community.
However, limitations in the III-V material system highly motivated the exploration of other materials. Among them II-VI materials have the most promising results particularly in detectors where high performance quantum well infrared photodetectors (QWIPs)\textsuperscript{84} have previously been reported. Like QWIPS, QCDs are quantum well based detectors that ISB transitions to absorb infrared light. These types of devices have been demonstrated in III-V materials for some time\textsuperscript{85}, but due to limitations in the conduction band offset and intervalley scattering, they are limited in their ability to operate at shorter wavelengths. The advantage of QCDs over the QWIP counterpart is that these photovoltaic devices are not as sensitive to noise born from current generation electronics. The II-VI ZnCdSe and ZnCdMgSe lattice matched material system promises to be an ideal alternative with which to develop short wavelength and low noise QCDs. In addition to a high conduction band offset of up to 1.12 eV\textsuperscript{75} and a higher electron effective mass ($m^*=0.13m_e$), these direct-band gap materials do not suffer from the carrier leakage into satellite valleys\textsuperscript{86} that often limit performance in strain-balanced III-V devices.

4.1.1 Novel II-VI Quantum Cascade Detector

In this section, the first II-VI QCD\textsuperscript{83} to be realized in the literature is presented. This device is an important technological milestone because of the reasons outlined above and there are great advantages for this material system. The II-VI QCD is a short wavelength IR device with the main transition centered at 4.1 $\mu$m (310 meV) from the e1 to e3 transition shown in figure 4.1a. Two secondary transitions at 417 meV and 530 meV are active. The structure extractor region is n-type doped to $\sim 3 \times 10^{17}$ cm$^{-3}$ shown underlined in the figure. The states are separated by about
one LO phonon to facilitate fast carrier scattering to the next well. The active region in the device was repeated 30 times, and superlattice fringes for this core region are clearly visible in HR-XRD (figure 4.1b). In this scan, we see sharp satellite superlattice fringes indicative of high quality material and well defined interfaces in the core of the device. The separation between these fringes allows us to calculate the period to 27.0 nm, close to the designed period of the device. The samples were then processed using standard lithography into 300µmx300µm windows.

Figure 4.2 shows the photocurrent spectra of the device as a function of temperature at zero applied bias and multi-pass FTIR measurements of the sample. The FTIR absorption measurement of transverse electric minus transverse magnetic measurements was taken by using a linear polarized filter and polishing the sample into 45° facets on both sides. The photocurrent
was measured with the device polished in a 45° wedge configuration (inset of figure 4.2b); illuminated from the glowbar source of a Fourier transform infrared (FTIR) spectrometer; chopped at 150 Hz; and detected using standard lock-in techniques. Two broad detection ranges can be observed from the figure. The first peak at 2826 cm\(^{-1}\) (E\(_{13}\)−350 meV), with a FWHM of 21%. A peak responsivity of about 0.1 mA/W, corresponds to a high BLIP detectivity of 2.5x10\(^{10}\) cm\(^{\sqrt{Hz}}\) W\(^{-1}\). The low responsivity is consistent with the high resistance of these devices at these temperatures.

4.1.2 Novel Broadband QCD II-VI Detector

Room temperature broadband intersubband detectors have become increasingly interesting as a platform for chip sized infrared spectroscopy. Existing intersubband IR detectors using III-V materials are limited in their wavelength coverage, and are therefore unsuitable for developing broadband detectors. This section describes the development of room temperature, high
performance QCD detectors using the II-VI material system. Shown in figure 4.3a is the design of the conduction band of the short wavelength core of the detector. The device is composed of three cores stacked on top of each other that detect a broad range of wavelengths. The schematic of the grown and characterized structure is shown in figure 4.3b. Three cores with designs similar to the short wavelength core are optimized 5.6µm, 7.0µm and 7.8µm. The layer sequence starting with the 5.6µm core is: \[44/24/15/20/18/20/22/20/26/20/32/14;\]
\[50/24/17/20/20/24/20/29/20/37/14\] for the 7µm core; and \[58/24/22/20/27/20/33/20/42/14\] for the 7.8µm core where the \(\text{Zn}_{0.51}\text{Cd}_{0.49}\text{Se}\) wells are given in normal font while the \(\text{Zn}_{0.29}\text{Cd}_{0.26}\text{Mg}_{0.45}\text{Se}\) barriers are in bold font. The underlined layers are doped to \(1\times10^{18}\) cm\(^{-3}\).

Room temperature photoluminescence measurements of samples etched with bromine-methanol reveal the underlying cores of the device (figure 4.4a). We can then see the optical properties of each core as well as the underlying contacts. From these measurements, an excitonic peak for ZnCdSe of 2.04eV is noted. This indicates that the composition of the wells in the structure are lower in zinc content than the lattice matched \(\text{Zn}_{0.51}\text{Cd}_{0.49}\text{Se}\) ternary. In addition, FWHM both
for both contact and all three cores are equal to ~80 meV, a linewidth larger than is expected for the best quality II-VI material on InP. HR-XRD measurements (figure 4.4b) confirm the PL results with a $\Delta a/a=0.67\%$ for ZnCdSe and 0.26% for the zeroth superlattice peak. However, we do observe sharp superlattice peaks indicative of sharp interfaces in the core from the superlattice interference fringes. Because of the complexity of the device and the broadness of the superlattice fringes, thickness cannot be extracted from XRD; as a result, XRR was used. From XRR measurements (figure 4.4c), we extract three periods, 29.7 nm, 29.1 and 28.8 for the 7.8 µm,

![Figure 4.4](image)

Figure 4.4 (a) Room temperature photoluminescence spectra measured by etching with a 2% bromine-methanol solution to expose the inner layers of the structure. (b) High resolution x-ray diffraction of the broadband QCD device. (c) X-ray reflectivity of the same device showing the period $s$ of all three cores.

Figure 4.5 Spectral response of the broadband quantum cascade detector showing the short wavelength core dominates the spectra.
7.0µm and 5.6µm cores respectively. These are larger than the designed wavelength likely due to a larger fraction of cadmium in the device rather than from calibrations. The spectral response from the device was a bit unexpected as most of the activity occurred in the short wavelength its core (figure 4.5). The peak responsivity of 5mA/W and a maximum operating temperature of 200K was achieved and a large spectral response range.

4.1.3 Novel Monolithic III-V/II-VI Quantum Cascade Detector

To further expand the performance range of broadband detectors, we propose to combine the two materials in a hybrid device structure. Specifically, we take advantage of a II-VI QCD device to span the 2-5µm range and couple it with a III-V QCD device for the 6-20µm portion. Presented here are monolithic hybrid QCD devices composed of a II-VI core with a peak responsivity of 5.1µm and a III-V core with a peak responsivity at 8.3µm as a proof of concept (figure 4.6). The hybrid devices respond with a range of 3.3-9µm at 80K. Two device designs are compared: one with a thick (600nm) InGaAs contact layer between the II-VI and III-V cores, used to address

Figure 4.6 (a) Conduction band design of the II-V short wavelength core and the III-V long wavelength core of a hybrid III-V/II-VI quantum cascade device. (b) Schematic diagram of two hybrid quantum cascade detectors grown and characterized.
each core individually (QCD 1); and one with a 200nm contact (QCD 2). The device with a thin middle contact layer (QCD 2) has improved performance with peak responsivity of 628µA/W compared to 57µA/W with the thick contact layer. Additionally, QCD 2 has a maximum detectivity of $1.4 \cdot 10^9$ cm$\sqrt{Hz/\omega}$ and a minimum noise current of $9.3 \cdot 10^{-15}$ A/$\sqrt{Hz}$. Illustrated in figure 4.7a, the x-ray diffraction scan of the (002) diffraction peak shows superlattice fringes from the two cores in QCD 1. Figure 4.7b illustrates the spectral responsivity for the two fabricated devices. Improvements in the hybrid material quality are currently being pursued to further optimize the device performance. These results are proof of concept that hybrid II-VI/III-V devices can greatly expand opportunities for novel device designs incorporating different material systems.

### 4.2 II-VI Disk Lasers

There has been a great deal of research and commercial interest in lasers in the visible range with high power and a high-quality output beam. Spectroscopic and commercial applications abound
should such devices be realized; for this reason there has been a push to unlock their potential for nearly twenty years. GaN based electrical injection ultraviolet lasers were the first to achieve the stability and performance necessary for them to become an integral part of today’s technology portfolio. However, despite a great effort on the part of numerous scientists there have been multiple difficulties when attempting to extend that success to lasers in the longer wavelengths of the visible range. The challenges stem from sacrifices in their material quality that must be indulged in when trying to create quantum wells that emit in the so-called “green gap” region. The appeal of high power lasers in this range stems from many factors including the sensitivity of the human eye, solar cell research spectroscopy and as the green component of white laser sources.

This section outlines research on a novel approach to achieve high power green lasers by utilizing a GaN ultraviolet pump down converted to the green utilizing a II-VI gain medium. Despite very high quantum efficiency of II-VI material systems, lasers yielded disappointing results despite early success, mostly due to difficulties with electrical transport across the devices. By taking advantage of the high quantum efficiency and eliminating electrical transport with the use of a GaN pump laser, it is apparent that the goal of green lasers is within our grasp. More specifically, InP based ZnCdSe wells with ZnCdMgSe barriers have been proven to be excellent candidates to achieve the elusive milestone. Not only is it feasible to produce high quality ZnCdSe/ZnCdMgSe green gain medium, but the system can be tailored across the entire visible spectrum. Additionally, other results in other components such as waveguides and distributed Bragg reflectors (DBRs) will be shown. These components provide the necessary material building blocks to produce II-VI green light emitting lasers. Disk lasers offer unique advantages
over injection lasers such as low divergence, circular high quality output beam and wide gain bandwidth ideal for short pulsed applications.

4.2.1 Growth of structures

The growth of these device structures was performed using the methods outlined in chapter 2 with the addition of growth interruptions as outlined in chapter 3. In exploring two different types of heterostructures, the first is green light distributed Bragg reflector (DBRs); a schematic of the structure is shown in figure 4.8a. The second, is a partial DBR with a laser gain medium atop of it (figure 4.8b). The design for the partial DBR laser structure (figure 4.8b) shows that the wells are separated at the maximum of the operating wavelength in the cavity. The number of wells is determined by the absorption coefficient of the active wells. The partial DBR anchors the wave so that the wells and wave maximum match, it also serves the purpose of giving the
structure strength when the substrate is etched away. There is also a small high bandgap layer inside the cavity to prevent exited electrons from leaking in to the substrate. In order to make complete laser structures (DBR, cavity and gain medium) three different Zn$_x$Cd$_y$Mg$_{(1-y-x)}$Se compositions were used. In the wells, lattice matched Zn$_{0.49}$Cd$_{0.51}$Se(2.1eV) for the active wells in the gain region was used. The three compositions used were Zn$_{0.42}$Cd$_{0.38}$Mg$_{0.20}$Se(2.5eV) for the low bandgap material in DBR; Zn$_{0.37}$Cd$_{0.33}$Mg$_{0.30}$Se(2.7eV) pump absorbing barrier material; Zn$_{0.25}$Cd$_{0.19}$Mg$_{0.56}$Se(3.0eV) carrier confinement material and DBR contrast layers. The two compositions for the DBR layers were chosen in order to give the greatest refractive index contrast while still maintaining quality, atmospheric stability and so as not to absorb the emitted light. Both heterostructures where capped by a thin Zn$_{0.49}$Cd$_{0.51}$Se layer to further prevent oxidation.

Figure 4.9: Scanning electron microscope image of the distributed Bragg reflector stack sample.
4.2.2 Distributed Bragg Reflector (DBR)

The DBR heterostructure stack (shown in figure 4.8a) was characterized using XRD (figure 4.10a), PL (figure 4.1b) and reflectance (figure 4.10c). In 2θ-ω scans of the (004) reflection we note well defined thickness fringes for the InGaAs buffer, indicative of a good heterovalent interface. We also note a lattice mismatch (Δa/a) of the zeroth order superlattice peak for the DBR stack to be less than 0.2%. The period of the DBR stack extracted from XRD scans is found to be 119nm. PL for the sample shows an excitonic peak of 2.54eV at 77K for Zn0.42Cd0.38Mg0.20Se and 3.13eV for the Zn0.25Cd0.19Mg0.56Se layers. A FWHM of 56 meV is observed for the Zn0.42Cd0.38Mg0.20Se layers consistent with good quality material. SEM measurements reveal clearly defined layers in the stack with the appropriate thicknesses for each layer (figure 4.9). Reflectance measurements show 84.2 percent maximum reflectance centered at 559nm, lower than simulated reflectance using Δn=0.285 diffractive index step. The lower value is likely due to the oxidation cap layer at the top of the structure and should not affect devices where this stack is incorporated.

4.2.3 Partial DBR Green Laser Heterostructure
A laser heterostructure incorporating 5 periods of the DBR device was grown and a schematic is presented in figure 4.8b. XRD, PL and SEM characterization were measured to determine the optical and structural properties of the sample (figure 4.11). In 2ω XRD scans of the sample, we also observed Pendellösung fringes as we did for the DBR sample cited in the previous section. Lattice mismatch in the entire structure was below 0.20% for all layers, though individual mismatch for the different layers is difficult to extract due to the complexity of the structure. SEM scans indicate that thicknesses of the layers are within 10% of the design specifications. PL measurements taken at 77K give an excitonic peak of 2.37 eV with a FWHM of 35 meV for the active wells in the structure. These results indicate good quality interfaces present in this device, although some improvement is possible as shown in the previous chapter for similar MQW structures. We also observed emission from all the different ZnCdMgSe compositions in the sample: 2.53 eV for Zn_{0.42}Cd_{0.38}Mg_{0.20}Se for the low bandgap material in DBR; 2.71 eV for Zn_{0.37}Cd_{0.33}Mg_{0.30}Se pump absorbing barrier material; and the wide-bandgap 3.03 eV Zn_{0.25}Cd_{0.19}Mg_{0.56}Se(3.0 eV) carrier confinement layer. These values are slightly lower than the designated 77K bandgaps.
Intensity-dependent PL measurements were carried out at room temperature using the second harmonic radiation (400nm) of a femtosecond Ti, sapphire laser and chirped- pulse regenerative amplifier system (Spectra-Physics Spitfire). The laser system generated light pulses of 130fs full-width-at-half-maximum (FWHM) duration, at a repetition rate of 1 kHz. The laser beam was incident on the sample at an angle of 45° to the surface normal, and the PL from the surface was collected in the back-propagation geometry along the normal to the surface by an optical fiber connected with the streak camera spectrometer (Imaging spectrograph G50is). A streak camera (Hamamatsu streak scope C4334) was used for time-resolved photoluminescence (TRPL) measurements. The streak camera temporal resolution is limited to 20ps. A 50 lines/mm grating was used in the spectrometer to observe the spectrum from 400nm to 600nm. The pump power of the second harmonic at 400nm was measured by a power meter (Spectra-Physics Model 407A).

Intensity dependent measurements of the PL spectra of the partial DBR green laser sample normal to the surface at room temperature. The results for sample A are shown in figure 4.12a,b. The surface PL is modulated by sub-cavity resonances, caused by the Etalon effect between the semiconductor/air interface and the InGaAs/DBR, indicated by the double peaks around the QW emission with a separation of about 20nm; this can be seen in figure 4.12a, and is for pump powers below 3mW when the main PL peak emission is at 539 nm; above 3mW, the PL emission at 548nm dominates. The PL intensity at 548nm increases at a much faster rate (higher slope) with pump intensity (figure 4.12b) above 3mW, while the luminescence at 539nm continues at a sub-linear rate throughout. The change in the slope of the PL intensity with pump power may be indicative of the onset of amplified spontaneous emission (ASE) or of stimulated emission; however, we have not decoupled the influence of an improving overlap between the
QW PL and a sub-cavity resonance with increasing pump power (and thus increasing temperature). Room temperature time resolved measurements were also performed for this sample pumped at 0.8mW; the decay times of the PL at 539nm and 548nm wavelengths were 1070ps and 616ps, respectively, as shown in figure 4.12c. With 3.0mW pump power, the decay times were 1106ps and 129ps, respectively, as shown in figure 4.12d. These results illustrate the potential of the ZnCdMgSe-based materials for fabricating optically pumped green light emitting SDLs.
Growth and Properties of Wide Bandgap \((\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m\) Short-period Superlattices

5.1 Summary

In this chapter, we explore the molecular beam epitaxy (MBE) growth and properties of \((\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m\) short-period superlattices (SPSLs) for potential application in II-VI devices grown on InP substrates. Wide bandgap \(\text{Zn}_x\text{Cd}_{1-x}\text{Mg}_{1-x-y}\text{Se}\) alloys can be grown lattice matched to InP with bandgaps ranging from 2.1 to 3.2 eV. Although good device properties have been reported with these alloys, the material quality degrades as the magnesium content is increased to obtain wider bandgaps (2.9-3.2 eV); and bandgaps higher than 3.2 eV are not usually achieved. SPSL structures up to 1µm thick with effective bandgaps ranging from 2.6 eV to above 3.42 eV are grown and characterized. Additionally, \(\text{Zn}_x\text{Cd}_{1-x}\text{Se}\) single and multiple quantum well structures using the SPSL barriers are grown and investigated. The structures are characterized utilizing reflection high-energy electron diffraction, X-ray reflectance (XRR), X-ray diffraction (XRD) and photoluminescence (PL). In our research, we observed layer-by-layer growth and smoother interfaces in the QWs grown with SPSL when compared to the \(\text{Zn}_x\text{Cd}_{1-x}\text{Mg}_{1-x-y}\text{Se}\) random alloy. The results indicate that this materials platform is a good candidate to replace the random alloy in device applications.

5.2 Introduction

One of the limitations encountered in the \(\text{ZnCdMgSe}\)-based devices described above is the possibility of achieving high quality lattice matched quaternary alloys with high Mg content and that yield bandgap above 3.0 eV. To circumvent that limitation, and to fully exploit the full bandgap range available from the materials system, we explored the use of...
pseudo-alloys or short period superlattices to substitute the random alloys. Short-period superlattices (SPSL), also known as digital alloys or pseudo alloys, are heterostructures of alternating binary or ternary alloys with periods of a few monolayers (ML), each whose properties resemble those of random alloys of similar composition. SPSL materials have been shown to be an attractive replacement for ternary and quaternary alloys in device applications due to their ability to suppress the propagation of defects as well as a highly advantageous ability to change alloy effective composition without source temperature changes during molecular beam epitaxy (MBE) growth. Recently, the wide-bandgap $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ material system lattice matched to InP has been shown to be an excellent candidate for several novel device applications. Green-light photo pumped lasers show promising results. Additionally, intersubband infrared devices based on this material system have shown the most advanced results outside the well-established III-V materials. Specifically, room temperature electroluminescence from quantum cascade structures has been demonstrated at 4.7 µm and 6.8 µm. Quantum well infrared photodetectors (QWIPs) with performance comparable to those made with III-V materials have also been reported. Indeed, II-VI based quantum cascade detectors (QCDs) and broadband QCDs perform as well as any reported QCDs in those wavelength ranges. However, devices from these materials are limited by the quality of a $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ component as we go to the wider bandgaps (2.9 to 3.2 eV); and, bandgaps higher than 3.2 eV are not usually achieved in sufficiently good quality. At higher bandgaps (>2.9 eV), $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ growth becomes difficult due to rock-salt phase transformations of the metastable MgSe component. We propose to replace the ZnCdMgSe barrier with short-period superlattices (SPSL) of ZnCdSe and MgSe to develop novel engineered materials.
Previously Shimbo et al\textsuperscript{100} investigated this system for visible light applications focusing on bandgaps below $\sim$2.85 eV. More recently, Chen et al explored the implementation of metastable MgSe barriers with a ZnCdSe spacer to provide the phase stability\textsuperscript{101}. This work demonstrates the possibility of wavelengths as short as 1.55µm in this material system, but the use of a spacer limits the types of devices that can be executed. Another key technological advantage of the proposed SPSLs is that in MBE growth abrupt changes in the bandgap of these materials can be changed by modifying the shutter sequence rather than changes in the beam flux necessary for ZnCdMgSe barriers.

Here a systematic investigation of the growth, structural quality and optical properties of (MgSe)$_n$(Zn$_x$Cd$_{1-x}$Se)$_m$ SPSLs with various period thickness presented. The long-term aim is to replace Zn$_x$Cd$_y$Mg$_{1-x-y}$Se in II-VI-based infrared, visible and terahertz devices lattice matched to InP. A comparison with Zn$_x$Cd$_y$Mg$_{1-x-y}$Se alloys of similar magnesium compositions is made. Novel (MgSe)$_n$(Zn$_x$Cd$_{1-x}$Se)$_m$ SPSL with bandgaps ranging from 2.52 to 3.42 eV are demonstrated and characterized. Grown structures are compared to simple Kronig-Penney model calculations\textsuperscript{30}. Quantum well structures utilizing SPSLs barriers were grown. Transfer matrix method (TMM) calculations were used to model these structures and predict the QW emission wavelengths. Simulations of conduction band designs using the envelope function approximation were also performed.

5.3 Experimental

The short-period superlattices of (MgSe)$_n$(Zn$_x$Cd$_{1-x}$Se)$_m$ layers near lattice matched to InP(100) were grown in a dual chamber Riber 2300 molecular beam epitaxy (MBE) chamber. For all
samples a lattice matched In\(_{0.47}\)Ga\(_{0.53}\)As buffer of \(\sim 128\)nm was grown on epi-ready (100) InP semi-insulating substrates to smooth the growth surface, and terminated with a 2x4 reconstruction to facilitate the heterovalent interface formation. The sample was then transferred via an ultra-high vacuum transfer system to a chamber dedicated to II-VI materials growth. A low temperature buffer layer was grown that involved 30 seconds of zinc flux exposure followed by a Zn\(_x\)Cd\(_{1-x}\)Se thin layer, both at a nominal temperature of 180°C. A detailed analysis of this growth procedure has been previously reported\(^{23}\). The substrate temperature was subsequently raised to 280°C and alternating layers of MgSe and Zn\(_x\)Cd\(_{1-x}\)Se were grown forming the SPSL. For bandgaps below 3.2 eV (samples 1-5), a Zn\(_{0.49}\)Cd\(_{0.51}\)Se lattice matched composition was used for the Zn\(_x\)Cd\(_{1-x}\)Se component; for the other samples, the ratio of Zn to Cd was adjusted so the SPSL was strain balanced. The total thickness of the digital alloys varied from 350-1000 nm and the MgSe/Zn\(_x\)Cd\(_{1-x}\)Se ratio was controlled by varying the number of monolayers. The structural details of each sample are summarized in table 5.1.

Table 5.1: Parameters of the various \((\text{MgSe})_n(\text{Zn}_x\text{Cd}_{1-x}\text{Se})_m\) short-period superlattices grown and investigated.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>n(ML)</th>
<th>m(ML)</th>
<th>XRD Period(Å)</th>
<th>SL t(nm)</th>
<th>(a_\parallel)</th>
<th>(a_\perp)</th>
<th>R(%)</th>
<th>(\varepsilon_{zz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>4</td>
<td>19.3</td>
<td>370</td>
<td>5.9072</td>
<td>5.8709</td>
<td>6.7</td>
<td>0.006</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>4</td>
<td>22.5</td>
<td>340</td>
<td>5.9501</td>
<td>5.8733</td>
<td>9.7</td>
<td>0.014</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>3</td>
<td>21.0</td>
<td>1000</td>
<td>5.9141</td>
<td>5.8983</td>
<td>78</td>
<td>0.007</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>2</td>
<td>18.6</td>
<td>1000</td>
<td>5.9111</td>
<td>5.8761</td>
<td>26</td>
<td>0.007</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>1.5</td>
<td>22.0</td>
<td>435</td>
<td>5.9417</td>
<td>5.8798</td>
<td>25</td>
<td>0.012</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>1</td>
<td>20.5</td>
<td>885</td>
<td>5.8695</td>
<td>5.8695</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>1</td>
<td>-</td>
<td>500</td>
<td>5.8695</td>
<td>5.8695</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>
5.4 Results and Discussion

During the growth of the samples, *in-situ* reflection high energy electron diffraction (RHEED) exhibited sharp and streaky patterns with a 2x1 reconstruction typical of high quality II-VI material for all samples (figure 5.1a-d). No significant change was observed throughout the growth of the samples. RHEED patterns, similar in sample 2 (figure a,b), were noted for samples up to 3.25 eV (samples 1-5 in table 5.1). Samples with bandgaps higher than 3.25
eV showed a modulation in the [110] streaky pattern (red circle in figure 5.1c), attributed to a reduction in the surface step length. This may be caused by the expected reduced surface mobility due to the stronger bond strength and relative size of the Mg in MgSe as compared with ZnCdSe layers, and perhaps mitigated by an increase in substrate temperature when growing the higher bandgap (MgSe)\(_n\)(Zn\(_x\)Cd\(_{1-x}\)Se)\(_m\) SPSLs. Before the growth of each sample RHEED, intensity oscillations (figure 5.1e) were measured to determine the exact times needed to grow the required thicknesses of Zn\(_x\)Cd\(_{1-x}\)Se and MgSe. We observed very good surface recovery in the oscillations with each shutter sequence. The thicknesses of each period obtained by the RHEED intensity oscillations was then confirmed by an analysis of x-ray diffraction satellite peaks for each SPSL structure (figure 5.1f and table 5.1). This thickness was multiplied by the total number of periods to estimate the total thickness of the SPSL layer.

X-ray diffraction (XRD) scans were performed to determine overall quality, thickness, roughness and relaxation of the SPSLs. As described above the thickness of the SPSL was determined using high resolution 2Θ-ω scans utilizing an analyzer crystal (HR-XRD). These results were also verified with x-ray reflectance (XRR) and found to deviate less than 1%, and less than 3% from the measured thickness from RHEED oscillations. A representative XRD scan is shown in figure 5.1f. The overall quality of the film remained competitive with samples of bandgaps of 3.25 eV (samples 1-5) consistent with observations seen in RHEED. The roughness of the (MgSe)\(_n\)(Zn\(_{0.49}\)Cd\(_{0.51}\)Se)\(_m\) SPSL was compared to Zn\(_x\)Cd\(_{1-x}\)Se/Zn\(_x\)Cd\(_y\)Mg\(_{1-x-y}\)Se SPSL, currently in use in intersubband devices utilizing XRR. A typical XRR scan for one of the QW structures is shown in figure 5.3a.
We noted an improvement relative to equivalent bandgap alloy material. This improvement is attributed to the reduction in alloy broadening. By comparing the peak positions of the zero order superlattice peak in symmetric (004) and asymmetric (224) scans, we observed in plane relaxation (R) of 6.7%, 9.7%, 25%. In plane relaxation is defined here as:

\[ R = \left( \frac{a_0 - a_{\perp SL}}{a_0 - a_{SL}} \right) \cdot 100 \]  

where \( a_0 \) is the lattice constant of InP, \( a_{\perp SL} \) is the measured in-plane lattice constant from (004) scans of the superlattice; and \( a_{SL} \) is the lattice superlattice lattice constant taken from the average of in-plane and out of plane measurements. The R value for samples of approximately 400 nm (samples 1, 2, 5) despite lattice mismatch ranging from 0.3%, 0.72% and 0.70%. The data is summarized in table 1. Relaxation of 26% was observed for the 1000 nm (sample 4) despite a mismatch of 0.4%. This shows a significant increase in the critical thickness when compared to the Zn\(_x\)Cd\(_{1-x}\)Mg\(_{1-y}\)Se random alloy of similar lattice mismatch, as also noted by others in (Si)\(_n\)(SiGe)\(_m\) SPSLs\(^{96}\). This observation is of importance in magnesium containing II-VI alloys where strain induced transformation to rock salt limits the realization of good quality material and devices\(^{99}\), especially as the magnesium fraction increases. However, as the magnesium fraction increases, the strain tolerance of the SPSL decreases. Strain values (\( \varepsilon_{zz} = \left( \frac{a_0 - a_{\perp SL}}{a_0} \right) \)) below 0.01 were required to grow good crystalline quality material when the magnesium fraction exceeded 75%. This was achieved by strain balancing the composition of the Zn\(_x\)Cd\(_{1-x}\)Se component, as done in samples 6 and 7. The significance of these results is that, even if strain is very low for the Zn\(_x\)Cd\(_y\)Mg\(_{1-x-y}\)Se random alloy, the crystalline quality of attempted samples beyond 3.1 eV is very poor, while highly effective bandgaps can be achieved with high quality in the SPSLs.
Table 5.2: Elemental composition of metals in short period superlattices and their calculated and measured bandgap energies.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Mg%</th>
<th>KPCalc. Eg(eV)</th>
<th>Measured Epk(eV)</th>
<th>FWHM PL(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.38</td>
<td>2.60</td>
<td>2.565</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>2.73</td>
<td>2.788</td>
<td>134</td>
</tr>
<tr>
<td>3</td>
<td>0.64</td>
<td>2.88</td>
<td>2.940</td>
<td>140</td>
</tr>
<tr>
<td>4</td>
<td>0.69</td>
<td>3.08</td>
<td>3.102</td>
<td>143</td>
</tr>
<tr>
<td>5</td>
<td>0.8</td>
<td>3.27</td>
<td>3.248</td>
<td>211</td>
</tr>
<tr>
<td>6</td>
<td>0.87</td>
<td>3.33</td>
<td>3.334</td>
<td>213</td>
</tr>
<tr>
<td>7</td>
<td>0.90</td>
<td>3.39</td>
<td>3.419</td>
<td>197</td>
</tr>
</tbody>
</table>

Photoluminescence (PL) measurements were performed to determine the optical quality and bandgap dependence of \((\text{MgSe})_n(\text{Zn}_{0.49}\text{Cd}_{0.51}\text{Se})_m\) SPSLs that were grown. Good optical quality material was achieved for all the samples with the room temperature PL peak energy ranging from 2.07 to 3.45 eV (figure 5.2a). We also observed full-widths at half maximum (FWHMs), plotted as the FWHM divided by the peak energy (or \(\Delta E/E\)), consistent with values reported for \(\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}\) random alloy samples of similar bandgaps up to 3.1 eV grown under optimized conditions.

Beyond a peak energy value of 3.1 eV we noted a significant reduction in the \(\Delta E/E\) observed for the SPSL samples. This improved behavior indicates that while the FWHM for the random \(\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}\) alloy increases sharply at higher bandgaps, likely due to the formation of extrinsic defects, the SPSL at higher bandgaps behave similarly to that observed in the random alloy at lower bandgaps. Additionally, the PL intensity was greater for SPSL than for the random alloys, especially for larger bandgaps where defect-related below bandgap emission dominates the spectra. We suggest that the improvement of the
optical properties at high bandgaps is due to ZnCdSe acting as a recovery layer for dislocations therefore reducing formation of rock salt domains seeded by dislocations in the SPSL. By calculating the effective bandgaps utilizing Kronig-Penney calculations, using $m_{cb}=0.23$, $m_{ev}=0.13$, $m_{hwh}=0.42$, $m_{hbb}=0.67$ and a conduction band offset of 1.12eV, and taking strain into account, we obtain good agreement, with deviations of less than 60meV, to the measured values (table 5.1). Additionally, there is good agreement to the fit

$E_g(\text{peak})=2.07+1.49x'$ (figure 5.2b) where $x'$ is the MgSe composition and 2.07 is the room temperature peak energy of the $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ component. This allows us to determine the ratio of $(\text{MgSe})_{x'}$ to $(\text{ZnCdSe})_{1-x'}$ needed for a given bandgap.

Figure 5.2: Photoluminescence spectra(a) at room temperature for SPSL samples showing the change in FWHM and bandgap with a change in MgSe and ZnCdSe ratio. (Inset) FWHM vs peak energy of SPSL samples shown in blue dots, and $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ shown in red dots. The red line is the best fit to the data of the $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ samples (small red dots). We note a deviation of the SPSL data (large blue dots) to this line at high peak energies. (b) The dependence of the MgSe fraction (equal to $d(\text{MgSe})/d(\text{MgSe}+\text{ZnCdSe})$) to the photoluminescence peak energy for SPSLs shown as red dots, and best fit to peak energy dependence in $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$ samples.
Single(SQW1 and SQW2) and multiple quantum well(MQW) samples utilizing
(MgSe)$_n$(Zn$_{0.49}$Cd$_{0.51}$Se)$_m$ SPSL as the barrier and Zn$_{0.49}$Cd$_{0.51}$Se as the well layer
material were grown to establish their potential for use in devices and to develop a model
that could be used to simulate device designs. XRR measurements of a MQW sample
(figure 5.3a) suggest interfaces superior to those of similar MQW samples grown
previously using quaternary random alloy barriers. A period of 1.93 for the SPSL barrier
superlattice and a period of 31nm for the MQW were extracted from the XRR

Figure 5.3: (a)XRR spectra of MQW sample using a SPSL as the barrier, a period of 1.93
for the SPSL and 31.31 for the MQW can be extracted. Very good interfaces denoted by
sharpness of interference fringes can be observed. (b)Photoluminescence spectra of a
MQW and two SQW samples showing a peak energy of 2.433 eV with a FWHM of 43
meV for the MQW, 2.426 eV with a FWHM of 53 meV for SQW1 and 2.303 with a
FWHM of 46 meV for SQW2. (c)Envelope function approximation simulations of the
conduction band for MQW, SQW1 and SQW2.
measurement. In 77K PL measurements we observed peak energies of 2.433 eV, 2.426 eV and 2.303 eV with a FWHM of 43 meV, 53 meV and 46 meV for MQW, SQW1 and SQW2, respectively. The MQW and SQW1 samples have similar quantum well and barrier designs (figure 5.3c) with the exception that in the MQW, the quantum well was repeated 30 times. We note that the FWHM is not greater for the MQW sample, suggesting that there is good reproducibility of thicknesses throughout the MQW structure. The line-width for the SPSL MQW structure is like that achieved with Zn$_x$Cd$_y$Mg$_{1-x-y}$Se barriers under optimal conditions (43meV). We also observed that changing the barrier height (by changing the SPSL period as was done in SQW2) is possible without any change in source temperatures, a technological advantage of this approach. Additionally, transfer matrix method (TMM)$^{30}$ calculations were performed utilizing the same parameters as in the Kronig-Penney calculations above, yielding bandgaps of 2.439eV for the designed 22Å wells (MQW and SQW1) and 2.319 eV for 26Å wells (SQW2), which are within 20meV of the measured values (figure 5.3b). The good agreement suggests that this modeling method can be used for design of optical devices.

5.5 Conclusions

Our investigations have confirmed that (MgSe)$_n$(Zn$_{0.49}$Cd$_{0.51}$Se)$_m$ SPSLs are good candidates to replace the Zn$_x$Cd$_y$Mg$_{1-x-y}$Se random alloy in InP based II-VI devices and applications. We have shown that good quality material with higher effective bandgaps can be achieved with these SPSLs rather than with random alloys. There is a significant improvement in the quality of the wider bandgap materials utilizing SPSLs. In the QWs grown using the SPSL as barriers establish the potential for the use of these materials in the design and growth of
novel high performance devices, such as infrared detectors and others. These findings may
be applicable to other metastable systems in which strain induced phase transformations are
problematic in realizing a given material; they also provide a tool to explore novel
metastable phase materials previously not observed.
Chapter 6: Bi$_2$Se$_3$/II-VI Heterostructures

6 Bi$_2$Se$_3$/II-VI Heterostructures

The molecular beam epitaxial (MBE) growth conditions of the II-VI semiconductors that we have investigated in the first part of this thesis are compatible with or similar to those of the novel Bi$_2$Se$_3$ materials and other topological insulators that we have also begun to research. Because of these similarities in conditions and as a natural extension of the concepts of hetero-epitaxy that underline this work we have explored the growth of heterostructures of these two types of very dissimilar materials. In this chapter, we look at “hetero-crystalline” materials combining Se and Te II-VI semiconductors based and topological insulator Bi$_2$Se$_3$ layers. The MBE growth of heterostructures of II-VI and Bi$_2$Se$_3$ is presented as a platform for band engineering so as to access TI surface states. Heterostructures such as Bi$_2$Se$_3$ with ZnCdSe, ZnCdMgSe, ZnSe and CdTe have been grown and characterized. Issues related to the growth of the coherent materials with different crystal structures and compositions will be explored. Additionally, we assess the control of polymorphism utilizing temperature and interfacial layers in the overgrown II-VI layers.

6.1 Wurtzite ZnSe, ZnCdSe and ZnCdMgSe on Bi$_2$Se$_3$

As described in the preceding chapters, heterostructures with varying degree of differences between the two component materials give rise to limitless opportunities in designing new materials that exhibit novel physical phenomena or that can have new and unique device applications. So far we have discussed heteroepitaxy of isovalent materials (i.e., ZnCdSe/ZnCdMgSe) and heteroepitaxy of heterovalent materials (i.e., ZnCdSe/InGaAs/InP). In this chapter we expand the concept of heteroepitaxy to include heterocrystalline materials, that
is, materials that exhibit totally different crystal structures (i.e., Bi$_2$Se$_3$/II-VI heterostructures). In this section, we investigate the molecular beam epitaxy growth of II-VI selenide semiconductor–Bi$_2$Se$_3$ heterostructures using c-plane sapphire substrates. Since the surface energy of Bi$_2$Se$_3$ is lower than that of the II-VI layers, their overgrowth is difficult and must be achieved in high quality before superlattices or heterostructures can be realized. Our studies demonstrate that Zn$_{0.49}$Cd$_{0.51}$Se and Zn$_{0.23}$Cd$_{0.25}$Mg$_{0.52}$Se layers exhibit improved quality relative to ZnSe layers. The structures exhibit a large relative upward shift of the TI bulk quantum levels when the TI layers are very thin (~6nm), consistent with quantum confinement imposed by the wide bandgap II-VI layers. Our transport measurements show that the characteristic topological signatures of the Bi$_2$Se$_3$ layers are preserved.

6.1.1 Experimental

The materials discussed in this section were grown utilizing the techniques and methods described in chapter 3. Bi$_2$Se$_3$ layers were grown in a chamber dedicated to the growth of these materials as described previously, and then transferred via UHV transfer modules to a chamber dedicated to II-VI materials. The steps for growth were as follows: first, 6nm Bi$_2$Se$_3$ was grown on the sapphire substrate and then transferred to the II-VI chamber for the growth of Zn$_x$Cd$_{1-x}$Se and Zn$_x$Cd$_y$Mg$_{1-x-y}$Se with compositions calibrated to be lattice matched to an InP substrate; there, II-VI samples were grown - one with ZnSe on top (sample 1), one with Zn$_x$Cd$_{1-x}$Se (sample 2), and one with Zn$_x$Cd$_y$Mg$_{1-x-y}$Se (sample 3).
6.1.2 Results and Discussion

Results of 2θ-ω (006) HR-XRD scans show that the Bi$_2$Se$_3$ initial layer remained intact and exhibited Pendellösung fringes (figure 6.1a). These fringes indicate that those layers of Bi$_2$Se$_3$ are of high quality of Bi$_2$Se$_3$ and that the interface between the II-VI and the Bi$_2$Se$_3$ layer is well ordered. A period of 9.3nm was extracted from the XRD scan. Similar results were obtained for all three samples. In-situ RHEED observations show a 1x1x1 pattern confirming (100) symmetry of the Bi$_2$Se$_3$ layer (figure 6.1c). Streaky patterns were observed for this layer indicating that the layer is of high quality. RHEED studies of the overgrown II-VI layers show six-fold symmetry and pattern characteristic of a metastable wurtzite crystal (figure 6.1c, d). The patterns observed showed spottiness (indicated in red circles); this indicates that three-dimensional growth took place for the II-VI layers. In order to verify the phase of the II-VI crystal, pole figures were taken for the hexagonal [102] plane (figure 6.1b) and we note a six-fold pattern at 37.97° for 2θ and 43.42 for φ, matching wurtzite ZnCdMgSe layers\textsuperscript{102}. Similar pole figures were obtained for

![Figure 6.1](image-url)
samples 1 and 2. Stabilization of wurtzite phase of II-VI magnesium containing compounds may open new applications in device design.

HR-XRD scans 2θ-ω scans along the (002) reflection show the lattice constant of each of the II-VI layer composition that was grown (figure 6.2a). From these scans calculation of the a-plane lattice constant yields 3.98Å for sample 1(ZnSe), 4.15Å for sample 2(ZnCdSe) and 4.13Å for sample 3(ZnCdMgSe) if we assume all layers are fully relaxed. This data indicates that there is a lattice mismatch of (0.3%) for sample 2 and (-0.3%) for sample 3 with Bi₂Se₃ (4.14Å), while sample 1 has a lattice mismatch of -3.9%, which may adversely influence the properties of the film. Rocking curves of the same (002) plane yield FWHM 1.72° for sample 1, 1.22° for sample 2 and 1.16° for sample 3 (figure 6.2b). The narrowing of the rocking curves indicates that material quality improves for the two layers that are near lattice matched to Bi₂Se₃. We also note that rocking curves are still relatively broad suggesting that improvements are possible. Growth of higher quality II-VI material on Bi₂Se₃ will be presented later in the chapter. Magneto resistivity(MR) measurements (figure 6.2c) were taken for these samples by contacting the Bi₂Se₃ layers directly in a van der Pauw configuration at 1.12K. We find the hallmark of weak-

Figure 6.2 (a) 2θ-ω scans of the (002) reflection of II-VI layers in sample 1, 2 and 3 (b) Rocking curves of the same samples along the same reflection. (c) Normalized magneto resistance of sample 1 and sample 3 measured in the van der Pauw configuration (inset).
anti localization can be interpreted as deriving from the topological surface states of the Bi$_2$Se$_3$\textsuperscript{103}.

### 6.1.3 Conclusion

Ordered crystalline layers of II-VI semiconductors were obtained by MBE on (100) plane Bi$_2$Se$_3$ layers deposited of sapphire. The II-VI materials overgrown on Bi$_2$Se$_3$ exhibit higher crystalline quality when lattice matching to the Bi$_2$Se$_3$ is achieved. Under the growth conditions employed, metastable wurtzite phase II-VI material was obtained. Evidence for quantum confinement effects were demonstrated, and weak anti-localization cusp in MR suggests that the topological surfaces of the Bi$_2$Se$_3$ were preserved. Superlattices of II-VI and Bi$_2$Se$_3$ may be possible and present a new platform for exploration of topological insulators.

### 6.2 Bi$_2$Se$_3$/ZnCdSe Superlattices

In this section, we explore the growth of Bi$_2$Se$_3$/Zn$_x$Cd$_{1-x}$Se superlattices. Since in a superlattice there will be multiple “surfaces”, the anticipated contribution from the surface states should be multiplied and easily accessed in charge transport, or in optical measurements if the topological properties of the interfaces are preserved. Near lattice matched Zn$_x$Cd$_{1-x}$Se was chosen to combine with Bi$_2$Se$_3$ as it yielded the best results, as illustrated in the previous section, and has a wide bandgap of $\sim$2.1eV.
6.2.1 Results and Discussion

Results for one sample comprised of seven periods of alternating layers of 11nm Bi$_2$Se$_3$ and 11nm of ZnCdSe lattice matched to Bi$_2$Se$_3$ are presented here. In comparing RHEED images of the bottom surface and the top surface of the superlattice (figure 6.3a), we can see that good recovery of the Bi$_2$Se$_3$ surface is achieved in this structure. In HR-XRD measurements we can identify the (006) and (009) reflections of Bi$_2$Se$_3$ as well as the superlattice zero order peak in the heterostructure. Thickness fringes for the superlattice are also visible confirming the period of

Figure 6.3 (a) Reflected high energy electron diffraction of the bottom and top layers of bismuth selenide and ZnCdSe in seven period superlattice (b) 2θ-ω scans of the (006 and 009) reflection of Bi$_2$Se$_3$ and the superlattice zero order peak in the heterostructure. (c) X-ray reflectivity scan of same sample.
22nm. From XRR measurements we can extract the thickness of the entire structure to be 158nm, close to the calculated 154nm expected. Curiously the superlattice period cannot be extracted from the XRR scan indicating the possibility of some inconsistencies in thickness across the sample. In transmission electron microscopy images, we see very sharp interfaces between the Bi₂Se₃ and ZnCdSe interfaces (figure 6.4a). We note, however, in lower magnification images (figure 6.4b) that the Bi₂Se₃ becomes thinner as we move up the structure, thus explaining the XRR results.

Measurements including Shubnikov de Haas (SdH) quantum oscillations (figure 6.5a, b) and Magneto conductance (figure 6.5c) were observed in the superlattice. We can fit the magneto conductance data to 2d transport theory and analysis of this fit will yield the number of channels
being measured\(^65\). Thus, we get an \(\alpha\) value of 3.62, close to 3.5 that would indicate 7 quantum channels in the sample. This indicates that 14 quantum channels would be active as is the number of surfaces; yet, charge transfer from the ZnCdSe cations at the upper surface of Bi\(_2\)Se\(_3\). This observation is consistent with DFT calculations of that surface. In SdH measurements we observed that fits to the minima of \(\Delta \text{R}_{xx}\) and \(d \text{R}_{xx}/d(\mu_0H)\) plotted in figure 6.5b give us a \(\beta\) value of 0.5 indicating that the transport measurements are mostly probing the surface states and not the bulk layers.
6.3 Single Chamber vs Two Chamber Growth

The heterostructures above were all grown in a dual chamber MBE system. Now we turn our attention to how the quality might change if a single chamber is used instead. For both methods, we observed narrow and streaky unreconstructed RHEED 1×1×1 typical of high quality Bi$_2$Se$_3$. When comparing double crystal 2θ-ω XRD (figure 6.6) scans we note significant narrowing in the FWHM of both the II-VI and Bi$_2$Se$_3$ layers. We also observe Pendellösung fringes for the sample grown in a single chamber indicating that sharper interfaces were achieved without the UHV transfer. When comparing rooking curves of the two samples (figure 6.7) we note a slight narrowing of the FWHM from 97arcsec to 77arcsec in the single chamber system. These results indicate that higher quality material can be achieved with the additional control in a single chamber system.

6.4 Bi$_2$Se$_3$/CdTe Multilayers

As previously described, the surface energy relationship between the Se-based II-VI compounds and the Bi$_2$Se$_3$ is not favorable for the good epitaxial growth of the II-VI on Bi$_2$Se$_3$. To probe this,
we identified other II-VI semiconductors that may have a more favorable surface energy relationship with Bi$_2$Se$_3$. In this section, we explore the structural and electronic properties of MBE grown on Bi$_2$Se$_3$/CdTe heterostructures. These thin films allow for the study of a strain, epitaxial relationship in crystal growth, and multiple Bi$_2$Se$_3$ surface channel films. We observe a strong relationship between crystal quality and lattice constant in the overgrowth of Bi$_2$Se$_3$ on CdTe seen in reflected high energy electron reflectance and x-ray diffraction and reflectance. We also note the marked improved crystal structure of CdTe layers when compared to II-VI selenide/Bi$_2$Se$_3$ heterostructures described earlier in the chapter; this behavior is attributed to reduced surface energy contrast between the CdTe and Bi$_2$Se$_3$ layers. Additionally, we report magneto-resistance weak anti-localization consistent with preserved Bi$_2$Se$_3$ surface states. From these results, we conclude that this material system is a good platform for band engineering of heterostructures of the two materials.

Figure 6.7 Double crystal rocking curves of two superlattices grown with one chamber or two chamber MBE systems.
6.4.1 Introduction

This work details the first steps to realize Bi$_2$Se$_3$/CdTe as a novel system for study and heterostructure engineering. We present the MBE growth of multilayered hetero-crystalline structures of CdTe and Bi$_2$Se$_3$ as a new platform for semiconductor/Bi$_2$Se$_3$ heterostructures. We expect, as in previous work with ZnCdSe, ZnSe and ZnCdMgSe, that the chemical compatibility of Se and Te anions will facilitate growth. Additionally, the zinc blende phase of CdTe has an optimal growth temperature closer to that of the optimal growth temperature of Bi$_2$Se$_3$; this feature may suppress the formation of wurtzite/zinc blende phase mixtures observed in selenium based II-VI/ Bi$_2$Se$_3$ heterostructures. CdTe has the additional advantage of a reduced surface energy contrast, when compared with II-VI selenides, and is expected to facilitate layer by layer growth at the interface between the two materials improving the interfaces and yielding overall higher quality crystals. However, as compared with the ZnCdSe materials there is a large lattice mismatch between CdTe and the hexagonal face of Bi$_2$Se$_3$. Here, we present results on how to control these competing effects to achieve high quality II-VI material on Bi$_2$Se$_3$.

6.4.2 Experimental

Three samples (S1, S2, S3) were grown on sapphire(1000) (S2) and InP(111)B substrates (S1 and S3), respectively. In-situ reflection high energy electron diffraction (RHEED) was used to characterize the crystal surface during growth. High-resolution x-ray diffraction (HR-XRD) and x-ray reflectance (XRR) measurements were performed with a Bruker D8 Discover with da Vinci design. Transport measurements were preformed using a physical properties measurement system (PPMS). These samples were grown in a dual chamber system. For S1 and S3 with InP(111)B, the native oxides were removed with As overpressure in a third chamber configured
for III-V materials also connected to the UHV transfer mechanism. For S2, the epi-ready sapphire substrate was cleaned by heating at 600˚C for one hour before deposition. Samples were then transferred to the chamber optimized for the growth of Bi$_2$Se$_3$ where layers were grown at a nominal temperature of 270˚C. In order to promote nucleation on sapphire, sample 2 included a low temperature buffer of 1 ML of Bi$_2$Se$_3$ initially deposited at 110˚C and subsequently annealed at 270˚C with a Se overpressure. After Bi$_2$Se$_3$ growth, the samples were transferred for the growth of CdTe material deposited at a nominal temperature of 270˚C.

6.4.3 Results and Discussion

In all samples, RHEED patterns indicated improved initial nucleation of CdTe on Bi$_2$Se$_3$, (figure 6.8a), as compared with the Se based II-VI over layers presented previously in the chapter. We attribute this improvement to the reduced surface energy of the CdTe as defined by cohesive energy DFT calculations (figure 6.8c, see section 1.4 for calculation details). In S1, the observed zinc blende CdTe(111) RHEED pattern degraded after 8 ML (figure 6.8b), and remained poor for the remainder of the layer. Samples were then transferred to the TI chamber and Bi$_2$Se$_3$ was
overgrown on the CdTe. The Bi$_2$Se$_3$ grown over the thick CdTe layer (S1) showed evidence of an additional domain in RHEED. In S2 and S3 the CdTe layer was kept to 8 ML and no degradation was observed. Additionally, the overgrown Bi$_2$Se$_3$ did not show any evidence of multiple domains and was consistent with single layer Bi$_2$Se$_3$. The quality of both Bi$_2$Se$_3$ and CdTe layers was examined with the use of XRD showing clearly that the CdTe layers are (111) oriented zinc blende crystals. We also examined the quality of Bi$_2$Se$_3$ over layers grown on CdTe of different thickness and found that the second Bi$_2$Se$_3$ showed signs of a second phase (101) (figure 6.9 orange line). Magnetoresistance measurements support the conclusion that the topological nature of the surface states persist. Hall effect measurements gave carrier densities and mobilities comparable to those of similar thickness MBE grown Bi$_2$Se$_3$ single layers. These results suggest that Bi$_2$Se$_3$/CdTe heterostructures are an attractive platform for band engineering studies.

Figure 6.9 XRD 2θ-ω scans of S1(top), S2(middle) and S3(bottom) showing the improved quality of the II-VI layer in S1 and S2. An additional Bi$_2$Se$_3$ phase can be observed in S1.
Chapter 7 Bi$_2$Se$_3$ Virtual Substrate for II-VI Heterostructures

7 Bi$_2$Se$_3$ Virtual Substrate for II-VI Heterostructures

The marked improvement of the crystalline quality and the zinc blende structure of the CdTe layers grown on Bi$_2$Se$_3$ pointed us to the exploration of using these structures as virtual substrates for II-VI device structures, thus allowing the growth of these structures on typically unacceptable substrates, such as sapphire or even glass. In this chapter, we present results on the growth and characterization of optical quality multiple quantum well (MQW) structures of Zn$_x$Cd$_{1-x}$Se/Zn$_x$Cd$_{1-y}$Mg$_{1-x-y}$Se on an ultra-thin Bi$_2$Se$_3$/CdTe virtual substrate on c-plane Al$_2$O$_3$ (sapphire). Excellent quality highly oriented films in the (111) direction were achieved as evidenced by RHEED and XRD. We also observed room temperature and 77K PL spectra with peak energies of 2.407eV and linewidths of 56meV. Exfoliation of the structures is also possible due to the van der Waals bonding of Bi$_2$Se$_3$. Exfoliated films exhibit photoluminescence emission nearly identical to the supported film. Additionally, CER show good agreement with simulations of the multiple quantum well structure as well as evidence of excited state levels needed for II-VI photonic devices. These results open new avenues of research for substrate independent epitaxy and the possibility of ultra-thin electronics.

7.1 Introduction

The quality of epitaxial thin films of semiconductors is generally contingent on the chemical and structural compatibility of films. Traditionally, the dependence is mitigated by use of substrates with the same valency, crystal structure and lattice constant as the epitaxial film grown on top. Although very high crystallinity can be achieved by this method, the cost and properties of the substrate restricts future applications. Virtual substrates allow us to relax these limitations by forming a layer that stabilizes one or more of the restrictions so that high quality films can be
The first restriction to be targeted was lattice constant. In this early work, the need to grow germanium on commercially important silicon substrates required specialized procedures in order to deal with the lattice constant differences\textsuperscript{104,105}.

Figure 7.1 (a) a-plane lattice constant of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ as compared with a-plane(111) of several zinc blende II-VI and III-V materials. (b) Multiple quantum well (MQW) structure grown and studied. (c) The Bi$_2$Se$_3$ unit cell illustrating quintuple layers separated by Van der Waals gaps shown with arrows.

Two dimensional (2D) materials have shown great promise as virtual substrates because the inherent van der Waals bonding and typically low surface energy allow them to self-organize on many different templates in a process called van der Waals epitaxy (VdWE)\textsuperscript{106}. Indeed, the Bi$_2$Se$_3$ 2-d material used here has been grown via VdWE in high quality on many substrates such as Si\textsuperscript{107}, sapphire\textsuperscript{108}, SrTiO$_3$\textsuperscript{109}, InP(111a,b)\textsuperscript{110,111} and even amorphous silica or glass\textsuperscript{112,113}. In the growth of Bi$_2$Se$_3$, it appears that either a limited chemical interaction or a compatible crystal structure are the only requirements to achieving high quality layer growth. Therefore, if high quality films can be grown on top of Bi$_2$Se$_3$, or its alloys, most conventional substrate requirements can be eliminated. Van der Waals virtual substrates have been used to produce
GaAs on silicon\textsuperscript{105}, GaN on silicon\textsuperscript{114}, ZnO on mica\textsuperscript{115} and II-VIs on other substrates\textsuperscript{116,117} including amorphous glass and flexible polyimide\textsuperscript{118}.

In this chapter, the growth of II-VI multiple quantum well (MQW) structures on a Bi$_2$Se$_3$/CdTe virtual substrate on sapphire (figure 7.1b) is investigated. Bi$_2$Se$_3$ was chosen because it has been demonstrated on many substrates, has the required van der Waals bonding (figure 7.1c) and because of its good symmetry and lattice constant compatibility with available InP based II-VI structures used in our study. Sapphire was selected as a proof of concept substrate because of its well-known incompatibility to II-VI materials, relatively low cost and easy preparation. In this scheme, Bi$_2$Se$_3$ provides the substrate independence. The CdTe buffer provides zinc blende phase stability and an intermediate surface energy layer between Bi$_2$Se$_3$ and the selenium based II-VI MQW structure. Minimizing surface energy contrast is required to maintain 2-d growth\textsuperscript{19}. II-VI materials represent an excellent candidate for this approach; this is because the lack of commercially available II-VI substrates has restricted the growth to III-V substrates thus, introducing a heterovalent interface which may limit the crystalline quality below standards set by commercially available III-V materials. Despite the requirement of a heterovalent interface, there is great promise for the II-VI materials in photo pumped visible lasers\textsuperscript{90}, quantum cascade emitters\textsuperscript{119} and intersuband detectors\textsuperscript{83,84}. Additionally, a virtual substrate of an alloy of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ will encompass most of the II-VI selenides (figure 7.1a) allowing one to design van der Waals substrates for a lattice constant ideal for the device being produced.
7.2 Experimental

The samples presented were grown in a molecular beam epitaxy (MBE) Riber 2300 with bismuth, zinc, magnesium, cadmium, selenium and tellurium sources. Epi-ready 350µm c-plane sapphire substrates were prepared for epitaxy by heating them to a nominal temperature of 600°C so as to remove water and any impurities on the surface. The sample was then cooled to ~110°C where a 2 minute Bi\textsubscript{2}Se\textsubscript{3} low temperature buffer was grown. Subsequently, the sample was heated to a nominal temperature of 270°C and left to anneal for 5 minutes with a selenium over pressure; next, approximately 2 nm of Bi\textsubscript{2}Se\textsubscript{3} were grown followed by a 3 nm CdTe layer. Subsequently, alternating layers of 20 nm Zn\textsubscript{0.22}Cd\textsubscript{0.21}Mg\textsubscript{0.57}Se and 2.4 nm of Zn\textsubscript{0.51}Cd\textsubscript{0.49}Se were grown; this sequence was repeated 20 times (figure 1b). A Bi/Se beam equivalent pressure (BEP) ratio of 1:10 was used for the Bi\textsubscript{2}Se\textsubscript{3}, a Cd/Te BEP ratio of 1:3 was used for the CdTe buffer and a group II/Se BEP ratio of 1:8 was used for the MQW layers. Standard samples were grown on epi-ready InP(100) semi-insulating substrates with methods described elsewhere\textsuperscript{55}. During growth, the samples were monitored with reflection high energy electron diffraction (RHEED).

After growth, x-ray diffraction (XRD), photoluminescence (PL) and contactless electroreflectance (CER) studies were performed on the samples. XRD scans were obtained with a Bruker Discover diffractometer with a da Vinci configuration and double crystal optics to observe the crystalline quality. Photoluminescence measurements were attained by excitation with a 325nm He-Cd continuous wave laser, and the emitted light was collected by a Princeton instruments monocromator with a CCD detector. The CER spectrum was realized at room temperature with a setup described elsewhere\textsuperscript{120}. In CER the sample is placed in a condenser-like system consisting of a front wire grid electrode with a second metal electrode separated from the first electrode by insulating spacers. This setup allows one to apply an alternating field to the
sample for modulation. Plot of the ΔR/R vs energy yields a derivative-like spectrum that is much richer in information than conventional reflectance. Mechanical exfoliation of the II-VI layered structure was performed using the “Scotch” tape method commonly used for graphene, where adhesive tape is applied to the surface of the II-VI film and then peeled off.

7.3 Results and Discussion

RHEED patterns observed along the <-211> direction during the MQW structure growth (figure 7.2b) are consistent with patterns reported for c-ZnSe on GaAs(111)B and on Bi$_2$Se$_3$. To stabilize the zinc blende phase at an optimal growth temperature of 270°C, the growth of CdTe buffer is necessary as the wurtzite phase dominates mixed phase films of ZnCdSe and ZnCdMgSe as we have previously reported. Asymmetric 2θ-ω XRD scans were used to verify the crystal structure and no evidence of the wurtzite phase was found. In XRD, 2θ-ω scans of the (111) peak of the MQW superlattice (figure 7.2a) near the zero order peak demonstrate

Figure 7.2 (a) X-ray diffraction 2θ-ω scan of the (111) diffraction peak of the multiple quantum well(MQW) showing the zero order peak(SL(0)) as well as the superlattice satellite interference fringes. (b) Reflection high energy electron diffraction pattern observed during growth of the MQW. (c) Long angular range XRD scan showing the Bi$_2$Se$_3$ virtual substrate(003,006) peaks, the (111) SL(0) peak and the sapphire (006) peak.
clearly visible superlattice fringes. The calculated period from fringe separations is 22.8 nm in close agreement to the designed period of 22.3 nm. In extended angle 2θ-ω scans (figure 7.2c) we can observe peaks matching Bi$_2$Se$_3$(003 and 006), a peak matching sapphire(0006) and the superlattice zero(SL(0)) order peak.

Photoluminescence(PL) spectroscopy was then performed for both the MQW on the virtual substrate as well as a reference sample grown under ideal optimized conditions on an InP(100) substrate for comparison. We observed well behaved PL at 77K (figure 7.3a) with a peak energy of 2.407 eV and a full-width at half maximum (FWHM) of 56 meV. We also noted a low intensity deep level emission on the MQW on the virtual substrate, likely due to interface states or twinning. These results indicate that even though optical quality material has been achieved further optimizations in quality may be possible. The MQW sample was then exfoliated to remove the sample from the substrate entirely using the “Scotch” tape method. In comparing its

![Figure 7.3](image)

Figure 7.3 (a) 77K Photoluminescence (PL) spectra of a II-VI multiple quantum well(MQW) structure grown on a virtual substrate. Spectra of the virtual substrate MQW has an emission peak of 2.407 eV and a full width at half maximum of 56meV, deep level emission seen at 1.9 eV. (b) Comparison of PL emission from the MQW virtual substrate sample before and after exfoliation from the substrate showing similar properties.
77K PL emission to that of the sample on the substrate, we observed identical FWHM and intensity as before exfoliation (figure 7.3b). We did note a small shift in energy of ~5meV after removal from the substrate; this is likely due to compressive strain relaxation when the sample was freed from the substrate template. The result indicates that the MQW structure is preserved after exfoliation, and can be bonded to another substrate; or it can be used for applications that require the device to be removed from the substrate, such as in ultra-thin electronics.

CER spectroscopy (figure 7.4) was performed on the MQW sample and compared to transfer matrix method(TMM) calculations(inset) of the intended design structure. The experimental

Figure 7.4 Contactless electro-reflectance(CER) spectrum of a multiple quantum well(MQW) structure on the virtual substrate at 300K. A fit to the energy levels found in the scan is shown in blue. We observe the band to band ZnCdMgSe(barrier) transition. The MQW h1-e1, h2-e1, h1-e2 and h2-e2 transitions are also visible. (inset) Transfer matrix method(TMM) calculations of the multiple quantum well region shows the electron density of various energy levels in the structure.
curve (red) was fitted to a curve using the derivatives of a Lorentzian lineshapes, shown in the figure by the blue line. The dotted lines indicate the position of the transitions needed to obtain the fitted curve. The measured transitions were assigned to transitions obtained by TMM calculations. The peak at 2.977 eV is allocated to the ZnCdMgSe barrier matching the energy of the 300K PL of calibration samples (2.995 eV). The peak at 2.384 eV is assigned to the h1 to e1 transition of the wells in the MQW structure (2.384 eV) and agrees well with the room temperature PL emission peak (2.385 eV) and the TMM calculation (see section 1.4 for calculation details) results (2.382 eV). The h2 to e1 (2.532 eV), and h1 to e2 (2.654) transitions also agree well with TMM results (2.509 eV and 2.647, respectively). The observation of these normally parity forbidden transitions is attributed to the presence of an integral field originating in the Bi$_2$Se$_3$ buffer layer. The presence and origin of such a built-in field is currently under investigation. Interestingly, the peak at 2.834 eV is found to closely match the value of the h2 to e2 transition obtained from the calculations for the second energy level in the well (2.832 eV). The good agreement between the observed transitions and the calculated transitions for such a MQW system suggests that the virtual substrate method yields well-behaved MQW samples that will likely facilitate the design of II-VI intersubband devices. In general, from these results we presume that well-behaved device quality materials can be grown on these novel virtual substrates.

7.4 Conclusions

Successful growth of MQWs of ZnCdSe/ZnCdMgSe was demonstrated using a Bi$_2$Se$_3$/CdTe virtual substrate. XRD rocking curves display the high crystalline quality of the MQW structure. PL spectra at 77K for the MQW grown on a virtual substrate shows optical quality material. We
observe that the PL emission does not change after exfoliation. CER measurements show peaks corresponding to the ground state and excited state transitions of the QW, whose energies match closely with those anticipated for the design structure. These results confirm that device quality epitaxial II-VI device structures on arbitrary substrates can be grown by MBE using a Bi$_2$Se$_3$/CdTe virtual substrate. Other materials systems may also benefit from the design of analogous virtual substrates.
8 Conclusions and Outlook

Throughout this dissertation, we have presented results for two different material systems whose applications are realized through the engineering of heterojunction interfaces. We explored how improving these interfaces has allowed for the best results quantum cascade (QC) electroluminescence devices based on ZnCdSe/ZnCdMgSe alloys lattice matched to InP. We have also demonstrated how growth interruptions and modifications of the heterovalent interface support II-VI ZnCdSe/ZnCdMgSe QC detectors that rival in performance currently available in commercial devices without the optimizations afforded by large volume production. Additionally, visible light emitters in this same system have begun to show signs of a developing platform of true full color lasers and light emitters. Furthermore, a new material system has been developed in the research for this dissertation comprised of novel topological insulator materials and II-VI semiconductors. This system demonstrates new physical properties with the potential to lead to whole new classes of electronic, spintronic and quantum computational schemes. The use of virtual substrates to achieve optical quality substrate independent II-VI materials has also been demonstrated here. Linking these results together is the growth technology utilizing molecular beam epitaxy where the necessary control of interfaces makes them possible.

The critical question arises as to the future of these technologies. Such a query is limited by the application, lest it become simply a musing of the writer. Thus, we will indulge each application with a few projections that are immediately within reach with the hopes that the reader may pursue such goals.
We begin with II-VI materials, the basis of all projects within this dissertation. There are simple milestones that will allow commercial development of II-VI materials towards what has been accomplished in silicon and III-V semiconductors. The first of these does not involve MBE but rather single crystal growth methods that supplement MBE; this is the development of high quality II-VI native substrates. The development of such substrates would eliminate the need of heterovalent interfaces and should facilitate much higher crystal quality in MBE films. The second advancement, a difficult one, is to find a suitable p-type dopant in II-VI selenides. This discovery would support the creation of many devices that are not currently possible including the potential transformation in the efficiency and color quality of LED lighting. However, more than any other concern in the growth of II-VI materials is that of p-type doping; this dilemma has consumed the most resources with little success. This problem stems from a basic failure to find a suitable dopant due to the weak bonding energies of most ideal dopants, and because those whose bonding energy allows for incorporation, such as nitrogen, but excessively distorts the II-VI lattice. An approach far outside the common methods that have been used for III-V semiconductors are inevitably needed to overcome this barrier.

The next topic to briefly examine is that of ISB quantum cascade (QC) devices made of II-VI materials. Although great effort has been invested in this purpose, the II-VI QC laser device has yet to be realized. It has been demonstrated in this dissertation that II-VI materials have the best QC electroluminescence results of any material outside III-V semiconductors. However, evidence of gain in the active medium is yet to be achieved. Considering how the introduction of growth interruptions drastically affects performance, it is plausible to predict that further improvements in the active core, such as those presented by short-period superlattices, will lead
to a working device. Other than short wavelength devices, II-VI offer unique theoretical advantages in terahertz QC lasers such as room temperature performance; that should be explored. The second ISB device presented in this dissertation is the QCD device. Since this device is already realized with high performance, the best avenue of pursuit is to continue to optimize these devices to make them attractive enough so that industry will adopt them in commercial applications. These optimizations include extending the wavelength range, higher performance at room temperature and better fabrication methods. Another device of interest is the monolithic integration of a QC detector and laser with on-chip spectroscopy applications.

Topological insulator semiconductor heterostructures offer perhaps the most exciting potential for the future. Since the work completed for this dissertation, there have been further advancements in this field with In$_2$Se$_3$ being used as the semiconductor. We can envision that other hexagonal semiconductors will produce similar if not new results. Furthermore, tuning the parameters between Weyl-semimetals, topological insulators and insulators offers a broad parameter space for a new type of band engineering of Dirac cone based materials. Finally, applications of topological insulators and other Dirac cone based materials is quite limited to date and will no doubt develop into a plethora of devices in the coming years.

The final application presented in this dissertation is that of van der Waals virtual substrates as a platform for substrate independent semiconductor devices. Now that optical quality material has been achieved, this advance has the potential to offer substrate independence for ultra-thin electronics and integrated optical-electronic interconnects. However, some major obstacles relating to crystal quality need to be overcome before any of them can be realized. The first
obstacle, evident in the films presented here, is that of twining. Because these films grow on hexagonal substrates with weak bonding to the substrate, twining remains a significant obstacle. Advances in twining suppression and removal, such as those achieved in GaN devices, must take place before any practical applications can be realized.
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Publications


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