

**The Molecular Beam Epitaxy Growth and
Characterization of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se-InP}$
Quantum Cascade Structures for Operation
in the 3 – 5 μm Range**

by

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partial fulfillment of the requirements for the degree of doctor of philosophy,

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Abstract

The Molecular Beam Epitaxy Growth and Characterization of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se-InP}$ Quantum Cascade Structures Designed for Operation in the 3 – 5 μm Range

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The quantum cascade (QC) laser has captured the interest of researchers for almost three decades. In the early stages, researchers were very interested in proving the QC concept¹ proposed by Kazarinov and Suris in 1971. This new concept gave researchers hope that very bulky energy inefficient infra-red (IR) lasers would be replaced with ones that are very compact, tunable and portable. Since the proposal of the QC laser concept and its first demonstration by researchers at Bell Laboratories² in 1994, this technology has progressed to the point where it is now finding commercial applications in a variety of areas such as military counter measures, free space telecommunications, infra-red imaging and chemical spectroscopy.³⁻⁵ The success of this technology can be attributed to the coming of age of the techniques of molecular beam epitaxy (MBE) semiconductor growth and bandgap engineering.^{6,7}

Using MBE technology, the temperature of the source material can be stabilized by making use of a combination of proportional integral derivative (PID) controllers and thermocouple feedbacks. As a result, the material flux from the effusion cells can achieve stability better than (+/-) 1%. This flux stability together with a well-developed computer

controlled shuttering mechanism make it possible to grow multi-quantum well (MQW) structures with excellent layer thickness precision (mono-layer scale) and interface quality. This stringent control of material flux is also a tool that is used by MBE growers to vary the material compositions for the growth of lattice matched and strain compensated QC structures. Today, MBE stands out as one of the premier methods for growing high performing QC lasers.

The first successful demonstration of a QC laser² was done using the InGaAs/InAlAs-InP material system. This demonstration was then repeated a few years later using GaAs/AlGaAs-InP.⁸ These III-V material systems were extensively studied to establish their material parameters. Given that material parameters are critically important in the process of modeling QC structures, it is not surprising that early success was achieved using these systems. Today, the best performing QC lasers operate in the 4 – 13 μm range and are produced using lattice matched InGaAs/InAlAs-InP. In order to produce short wavelength QC lasers, the well layer thicknesses in the active region of the device must be reduced in an effort to push the lasing energy states further apart. This reduction in well thicknesses results in the movement of the upper lasing state closer to the bandedge. This action increases the probability of the lost of lasing state electrons to the continuum. Therefore, in order to produce high performing short wavelength QC lasers, a large conduction band offset (CBO) is required. The CBO of lattice matched InGaAs/InAlAs-InP is 0.52 eV. In an attempt to produce high performing devices below 4 μm many researchers have resorted to the use of strain compensation⁹⁻¹¹. This approach has yielded very little improvement in performance due to electron scattering to the X

and L intervalleys. This has lead to the exploration of wide bandgap material systems such as the antimonides and nitrides.

In this work the wide bandgap II-V $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se-InP}$ will be explored for QC laser fabrication. To this end, QC lasers were designed for operation at 3 - 5 μm range. A Matlab-based program was written to calculate the energy level spacing within the active region of these devices. This simulation program was based on Schrödinger's equation and the transfer matrix technique. Several calibration samples were grown to establish the doping levels and growth rate of the well and barrier materials. The growth rate was measured using scanning electron microscopy (SEM) and reflection high energy electron diffraction (RHEED) oscillations during MBE growth. X-ray diffraction measurements were performed to determine the lattice mismatch of the II-VI bulk layers, and therefore predict whether material composition adjustments were required to attain the lattice match condition. The samples that were grown were studied using photoluminescence (PL) to determine the bandgap of the well and barrier material. This information was then used to calculate the CBO of the II-VI MQW structure. In addition, PL studies were also carried out to look for material defects and assess the quality of the well/barrier interface. These II-VI QC samples were also subjected to Fourier transform infra-red (FTIR) absorption spectroscopy to determine the energy levels in the grown structures. After optimizing the active regions using simulation data and FTIR results, electroluminescence (EL) structures were grown and processed into QC emitters using a combination photolithography and electron beam contact deposition. The processed structures were then biased and investigated for IR emission at temperatures ranging from 80 K to room temperature.

To my family

Acknowledgments

This document represents the high point in my academic development. The journey to this milestone started with the guidance of my parents Theresa and Hamilton Charles. Very early in my life they instilled in me the belief that I could do anything if I committed myself to it. Everything that I am today can be attributed to the work ethics and values I gained from my family; for that I am eternally grateful. Special thanks to my sister, Linda Charles, for her support because without her my dream of attending college would not be possible. She supported me wholeheartedly in all of my academic endeavors up to the very end; therefore I dedicate this document to her.

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Chapter 1

Introduction

The quantum cascade (QC) laser is a novel device that has captured the interest of many individuals in the research community for more than two decades. This device has provided a wealth of opportunity for fundamental research advances as well as a promise of a high power infrared (IR) light source that could have a broad range of applications. Many of the chemical species found in the atmosphere such as chemical pollutants, human breath and products used in chemical and biological warfare have strong characteristic absorption lines in the mid-IR. Therefore spectroscopic devices equipped with laser sources that emit in 3-5 μm and 8-13 μm range are extremely important in, atmospheric pollution monitoring, medical research, and the war on terrorism. Additionally, these light sources could prove to be invaluable in military countermeasures, and point-to-point free space telecommunication.^{4,12-15}

To date, QC lasers in the mid-IR range are seen as a viable alternative to current solid state and diode lasers which are bulky energy inefficient devices. Through the use of band-structure engineering and molecular beam epitaxy (MBE)^{6,7}, QC lasers can be made into small compact devices that operate at temperatures that are significantly higher than the solid state or diode laser counterparts. Also, QC lasers have the added advantage of being widely tunable throughout most of the IR band.

Since the first QC laser was demonstrated by scientists at Bell Laboratories² in 1994, there has been a very intense research effort to increase the device output power in both pulsed and continuous wave (CW) mode of operation while expanding the emission

bandwidth. To date, the shortest and the longest operating wavelengths that have been realized are 2.75 and 150 μm , respectively.^{9,16,17} Also, the highest wall plug efficiency (the ratio of output to input power) of QC lasers at room temperature (RT) is in the range of 10 to 15 %.¹⁸⁻²⁰ This level of efficiency indicates that a significant amount of the injected electrons are not involved in photon generation. These inefficiencies may be due to the loss of electrons from the upper lasing states to the continuum because of a short conduction band discontinuity, ΔE_c . This performance limitation may also be indicative of poor injection efficiency as a result of band misalignment at the injector/active region interface. The inability of researchers to produce high performance devices that operate below 4 μm is a major concern for researchers performing spectroscopic studies in the 3-5 μm band. The principal reason for this shortfall is the relatively small ΔE_c of the InGaAs/InAlAs system that is currently used to produce mid-IR QC laser.

In order to overcome the problem of low output power and the 3.4 μm wavelength limit posed by InGaAs/InAlAs, new material systems must be explored. Currently, the III-V antimony-based type II system is being forcefully investigated. This material system is indeed a very attractive alternative because of the following:

- (1) The gain of QC lasers is inversely proportional to the electron effective mass in the material system that is used. Due to the fact that the electron effective mass of the antimonides is relatively small, very large gains are possible.
- (2) The ΔE_c is large enough to enable operation in the 3-5 μm window. In the case of InAs/AlSb ($\Delta E_c = 2.1 \text{ eV}$) ΔE_c is large enough for QC laser operation at wavelengths as short as the telecommunication wavelength of 1.5 μm .²¹

To date, the shortest reported operating wavelength of QC lasers made from this material system is about $2.75\text{ }\mu\text{m}$,²²⁻²⁴ however, the performance of antimonide-based QC lasers is still a major issue. The inability of researchers to produce highly performing QC lasers of shorter operating wavelengths may be due to a reduction in the effective ΔE_c because of electronic interaction between the Γ -X and Γ -L valleys of the antimonide material system. In the case of the InAs/AlSb, the Γ and L valley separation in the first Brillion Zone is $\sim 800\text{ meV}$, which is significantly less than the Γ - Γ value of $\Delta E_c = 2.1\text{ eV}$.²⁵ Because of the absence of a common anion, the growth of antimonide alloys has proven to be a challenging task.²⁶ This challenge has resulted in quantum well (QW) interfaces that are rough. This interface roughness results in QC lasers with increased line widths and reduced material gain. Unlike the antimonides, very uniform type I ZnCdSe/ZnCdMgSe QWs with high interface quality and ΔE_c as high as 1.12 eV can be easily grown lattice matched to InP substrates. Also, there are no intervalley interactions in these II-VI materials. As a result, the $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ II-VI material system is a very promising material system for producing a high performance device in the $3\text{-}5\text{ }\mu\text{m}$ window.

The following chapters of this thesis will be dedicated to discussing my efforts to develop the materials and structures needed to design and fabricate II-VI QC lasers: Chapter 2 provides background information on the II-VI material system, the MBE growth and the basic operating principles of the QC laser. Chapter 3 focuses on the various characterization techniques used in this work. Chapter 4 highlights previous work that sets the foundation for this thesis dissertation.

Chapter 5 is dedicated to giving information on the modeling of the active region of the QC laser.

Chapter 6 presents a detailed study of the active region of the first generation II – VI electroluminescence (EL) structure.

Chapter 7 provides details on the growth and processing of II – VI QC structures. In addition, photoluminescence (PL), x-ray, Fourier transform infrared (FTIR) and EL results for the first generation II – VI QC structure will be presented.

Chapter 8 presents the results for the optimized second generation QC structures.

Finally, in chapter 9 the results of this thesis dissertation are summarized. Also this chapter provides details on future directions of this research effort.

Chapter 2

Background

Over the past fifteen years our group at the City College of New York (CCNY) has perfected the art of growing $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ alloys on InP and GaAs substrates. In the initial stages, our research was motivated by the fact that the technology for producing high quality III-V (n-type and p-type) substrates was well established and II-VI alloys were structurally similar (zinc-blend) to these III-V substrates. Also, the idea of growing high quality $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ was of great interest to researchers because of the wide range of bandgaps spanning the visible range of the optical spectrum. This wide bandgap material presented the opportunity to explore production of multi-quantum well (MQW) devices such as blue-green lasers, red-green-blue LEDs and detectors visible light range. Over the years, interest in II-VI blue-green lasers has waned due to difficulty in achieving high p-type doping in this material system. This was further compounded by the fast progress achieved in this regard from the III-nitride materials. Today, there is a renewed interest in this wide bandgap material for the production of photonic devices emitting in the green, which are still not achieved by the nitride system. More recently, our group has also demonstrated that QWs made from these materials exhibit a very large CBO. This research is motivated by the fact that high quality $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ can be grown lattice matched to InP with a CBO as large as 1.12 eV. This large CBO provides the opportunity to produce high performance devices such as quantum cascade lasers (QC) within the 3 -5 μm range.

2.1 $\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ Material System

The II-VI material system, $\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$, has a zinc-blend structure similar to that of the III-V substrates (InP or GaAs) on which it is epitaxially grown. This II-VI alloy is composed of varying percentages of ZnSe, CdSe and MgSe therefore, forming an epitaxial whose composition could be manipulated to attain a lattice constant similar to that of the substrate (lattice-matched).

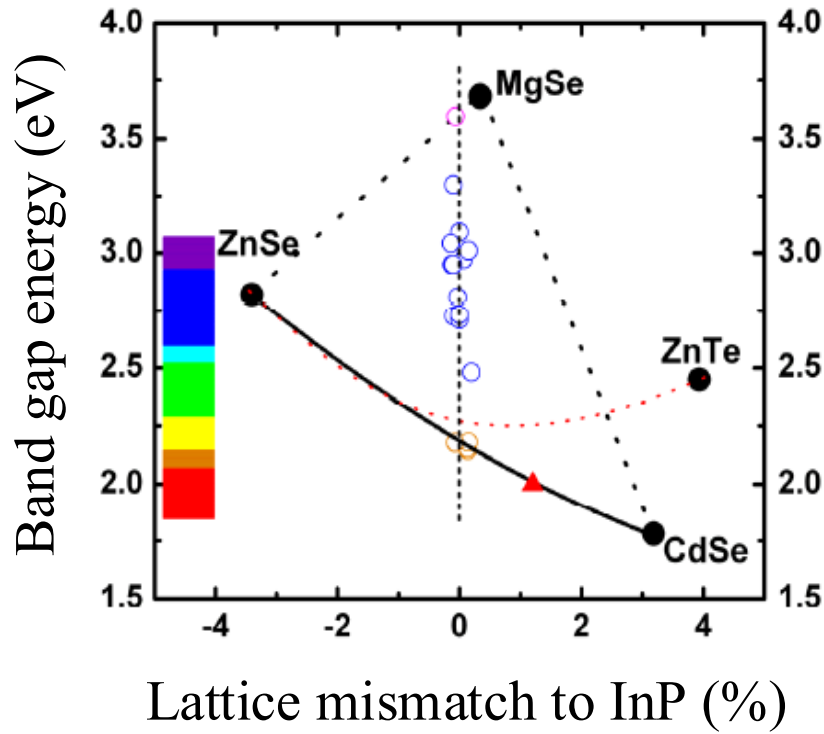


Figure 2.1: Graph describing the II-VI materials system. The solid circular points represent the binary constituents of the II-VI system. The points along the dotted vertical line correspond to ternary and quaternary compositions that are latticed matched to the InP substrate.

Figure 2.1 shows the bandgap as a function of lattice mismatch to InP for the ZnCdMgSe alloy system. The dark solid circles in this figure indicate the bandgap and the percentage lattice mismatch to InP of the binaries. The solid and dotted lines in Fig. 2.1 show the variation of the II-VI ternaries bandgaps with lattice mismatch. The solid line is also an empirical fit to data that was previously reported.²⁶ The spread of open circles on the vertical dotted line in the figure corresponds to the bandgaps of ternary and quaternary layers lattice matched to InP that were grown by our group. Our group has also demonstrated the growth of QWs with ternary wells and quaternary barriers that were lattice matched to InP. Using the contactless electro-reflectance (CER) technique, it was determined that the CBO of the grown quantum well is 82% of the difference between the ternary and quaternary material bandgaps.²⁸ To date, our group has demonstrated that CBO as large as 1.12eV can be attained using lattice matched alloys.²⁹ This CBO could be further extended by employing strain compensation. Hence, using this material system there exist the potential to produce QC devices that could operate throughout the mid-IR band.

2.2 Basics of Molecular Beam Epitaxy

2.2.1 Introduction

Molecular Beam Epitaxy (MBE) is one of several growth techniques used by researchers to produce epitaxial thin film semiconductor structures and devices. With MBE, the epitaxial layers can be deposited on the substrate to produce a variety of complex semiconductor heterostructures and devices. The substrate acts as a template for

the arrangement of the adatoms that are deposited ideally one monolayer (ML) at a time. With this technique, researchers are able to produce multi-quantum well (MQW) structures with excellent interfacial quality and thickness precision on the monolayer scale. The maturation of MBE meant that researchers finally had the tools to undertake the band-structure engineering that is critical for realizing complex devices such quantum cascade lasers (QCLs).^{6, 7}

2.2.2 Overview of the MBE System

The dual chamber MBE system that was used for growing the $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ MQW structures in this work consist of a metallization chamber and two growth chambers (with a chamber dedicated to III-V and II-VI materials respectively) that are all interconnected via a ultra high vacuum (UHV) transfer tracks (see Fig. 2.2). The III-V and II-VI chambers contain eight effusion cell ports each. The III-V chamber in our MBE laboratory is equipped with six effusion cells containing gallium (Ga), indium (In), arsenic (As), silicon (Si), beryllium (Be) and aluminum (Al). The Si and Be are used as n-type and p-type dopants respectively. The II-VI chamber on the other hand has 7 cells of which two contain zinc (Zn), and the another five cells contain cadmium (Cd), magnesium (Mg), tellurium (Te), selenium (Se) and zinc chloride (ZnCl_2), respectively. The eighth cell port contains a nitrogen plasma source that is used as the p-type dopant. The ZnCl_2 source is used as the n-type dopant. Figure 2.3 (b) shows a schematic diagram of the MBE chamber outlining all the major components.

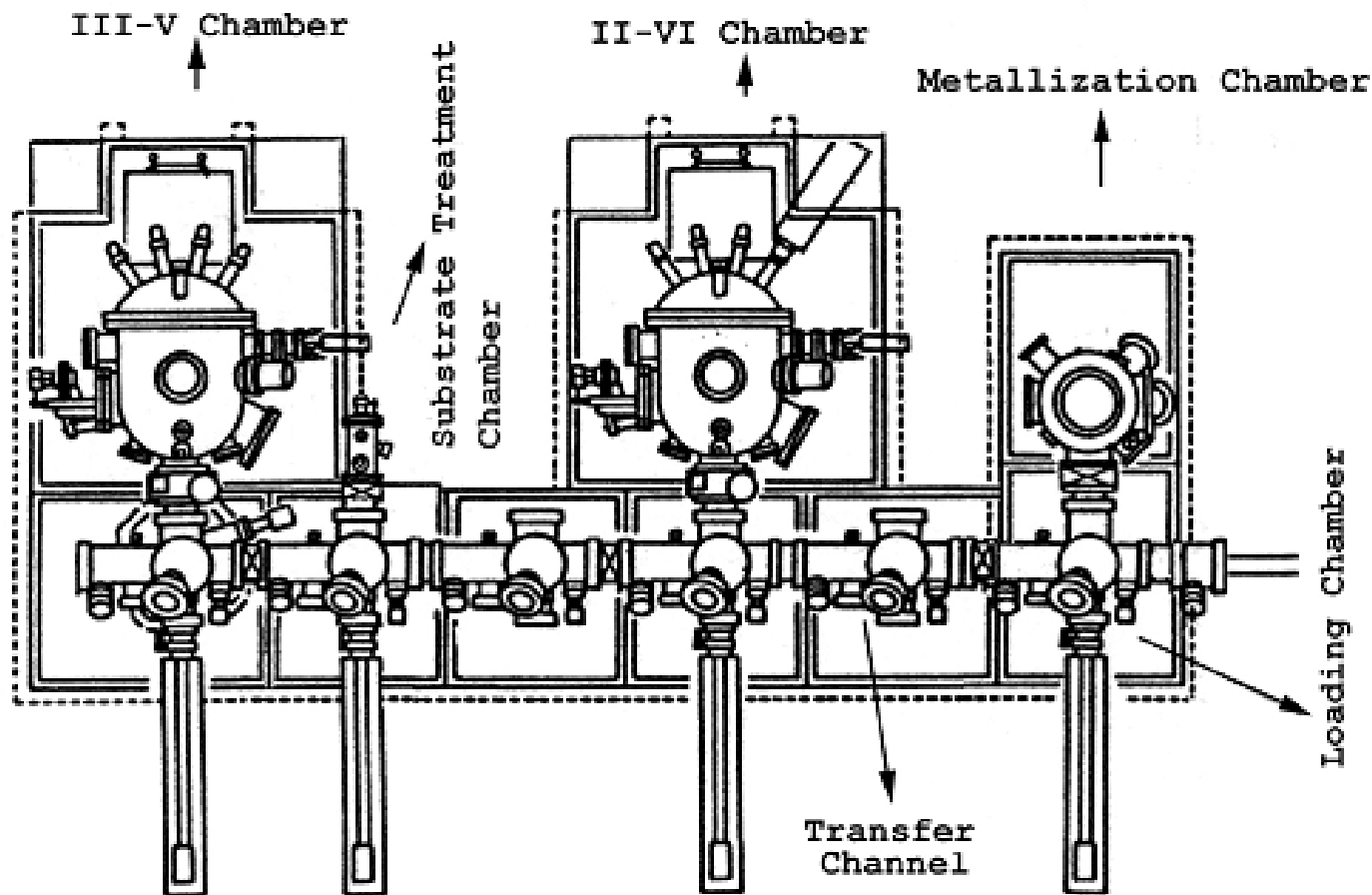


Figure 2.2: Diagram of Riber 2300 dual chamber MBE system with attached metallization chamber.

The MBE solid source effusion cells are equipped with a heating coil and thermocouple for heating and maintaining the source material at a desired temperature. With the use of proportional band integral derivative (PID) controllers and thermocouple feedback, the material flux from the effusion cells should be able to achieve stability of better than $(\pm) 1\%$. This is essential for maintaining the composition of the epitaxial layers that are deposited. Each effusion cell is equipped with a shutter that could be operated manually or with the help of an electronic shutter controller. These effusion cell

shutters make it possible to abruptly start or stop the beam of source material flowing onto the substrate. Therefore the shutters make it possible to start and stop the growth of a particular layer. This capability is critically important in fabricating multi-layers structures such as multiple QWs (MQWs) with uniform thickness and high quality interfaces.

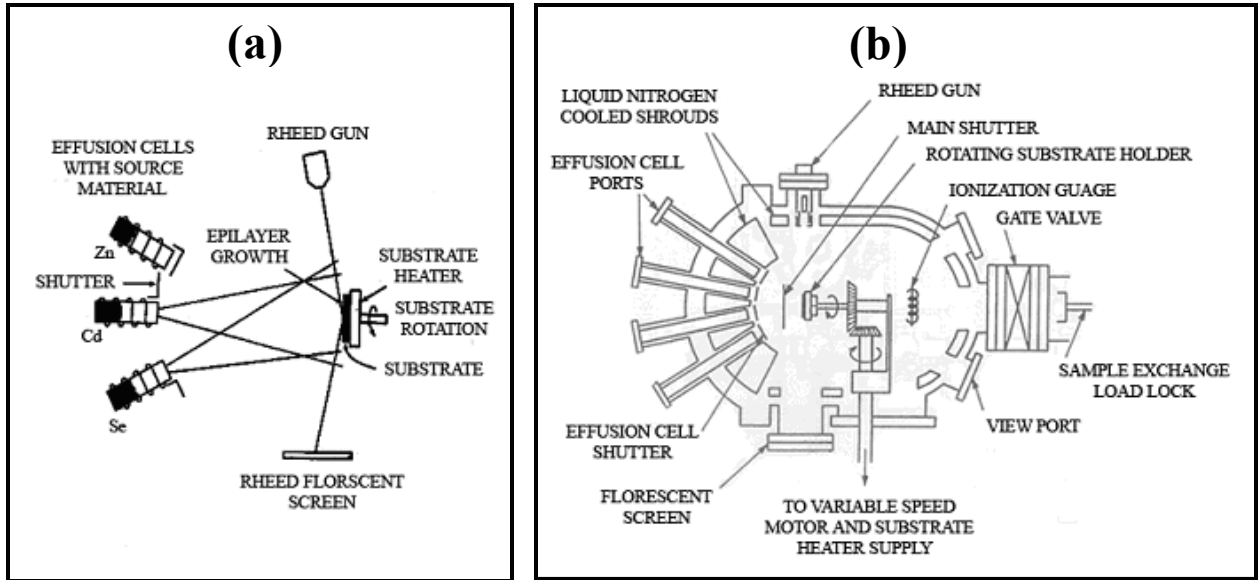


Figure 2.3: (a) Illustration of the MBE process and RHEED *in situ* grown monitoring. (b)

Schematic diagram of MBE chamber outlining all the principal components.

The growth chamber also contains a rotating substrate holder on which the substrate is placed (see Fig 2.3). The rotation of the substrate ensures thickness and compositional homogeneity of materials grown during the MBE process. Like the effusion cells, the substrate holder is equipped with a heater, thermocouple and the PID/thermocouple feedback circuitry for maintaining the substrate at the desired growth temperature. The MBE growth chambers and transfer modules are connected to very efficient cryogenic, turbo and ion pumps that serve the purpose of providing an ultra high vacuum (UHV)

environment where the pressure is 10^{-9} Torr and lower. During the MBE process, liquid nitrogen (LN_2) is allowed to flow through the LN_2 shrouds that line the wall of the MBE chamber. The cooling of the chamber ensures background particle adhesion to the chamber wall as a result of energy transfer during the chamber wall/particle collision process. This in turn leads to further improvements of the UHV condition. The UHV environment is of great importance because it ensures that particles that could scatter the beam of source material from the effusion cells and also contaminate the epilayer, are absent or kept to minimum. The UHV also serves the purpose of minimizing the scattering of the electron beam from the reflection high energy electron diffraction (RHEED) gun. Hence, this ensures that a sharp diffraction pattern can be obtained on the RHEED phosphor screen. The RHEED system is critically important in the monitoring of the sample quality during MBE growth. During MBE growth the sources are heated to a predetermined temperature to achieve a desired flux. When the shutters are opened, the flux is impinging on the substrate, which has also been heated to a desired optimum temperature. The basic concept is illustrated in Fig. 2.3 (a).

2.2.3 Pre-growth Sample Preparation

The pre-growth sample preparation is a very critical step in the MBE process. During this stage, the substrate on which the semiconductor epilayer is grown is mounted onto molybdenum (Mo) blocks using molten indium (7N). Sample preparation is done in class 100 fume hood where there are very few dust particles to contaminate the substrate surface and give rise to oval defect in the grown semiconductor epilayer. Before the sample is mounted, the Mo block must be thoroughly cleaned to minimize the generation

of contaminants particles when the block is heated in the growth process. To this end, the Mo block is first etched in a bromine/methanol solution for ten minutes to remove the semiconductor material that was deposited in the previous growth. This is then followed by a HCl:HNO₃ (1:1) etch to expose a clean metal surface. At the end of the chemical etch process, the Mo block is thoroughly rinsed under deionized water flow for ten minutes. Finally, the Mo block is placed in an ultrasonic bath of methanol for ten minutes to get rid water. At the end of this cleaning process, the Mo block is dried with nitrogen gas before it is placed on a hot plated. At this point the cleaved semiconductor material, which is purchased from the vendor having “epi-ready” pre-cleaning, is attached to the block using a film of molten indium. The substrate/block is then enclosed in a covered Petri-dish before it is removed from the fume hood and place in the MBE system. Mo blocks with mounted (001) InP substrates are usually stored in the UHV load-lock chamber for at least one day before it is transferred to the front of the III-V chamber via the transfer channel (or track).

2.2.4 Growth of Zn_xCd_(1-x)Se/Zn_xCd_yMg_(1-x-y)Se on InP Substrate

In order to grow the II-VI epitaxial layer, both the III-V and II-VI chambers are used. Liquid nitrogen is allowed to flow through the chambers for about 30 minutes at which time the background pressure in the III-V and II-VI chambers would be in the mid 10⁻⁹ and 10⁻¹⁰ torr, respectively. The effusion cells that will be used in the III-V growth are heated to the desired temperatures and allowed to stabilize for 15 minutes. Those used in the II-VI growth are brought up to the desire cell temperatures during a 30 minute time interval with the main and cell shutters closed. At the end of this cell heating period, the

cell shutters are opened and cell temperatures are allowed to stabilize for one hour. On completion of this heating process, the cell shutters are close in order to commence material flux measurements.

Flux measurements in the III-V and II-VI chambers are usually done according to the magnitude of the material flux used for growth. In order to repeatedly grow high quality InGaAs lattice matched to InP, flux ratios of $F_{\text{In}}/F_{\text{Ga}} = 2$ and $F_{\text{As}}/(F_{\text{In}} + F_{\text{Ga}}) = 50$ are usually used. The typical material fluxes that are used for InGaAs growth are $F_{\text{Ga}} = 1 \times 10^{-7}$ torr, $F_{\text{In}} = 2.0 \times 10^{-7}$ torr, $F_{\text{As}} = 1.5 \times 10^{-5}$ torr. Thus, flux measurement for this growth would be done in the following order: First Ga, next In and finally the As cell.

Flux measurement in the II-VI chamber is usually done as soon as the 30 minute heating and 60 minute temperature stabilization process is completed. This measurement is usually done in the following order: First Mg, next Zn, then Cd and finally the Se. The procedure for the measurement is as follows:

1. Open the main shutter and record the background pressure, F_{BG} .
2. Open the shutter for the Mg cell. Wait two minutes before recording the material flux, F_{Mg} . At the end of this two minutes close the Mg cell shutter.
3. After one minute of closing the Mg shutter record the background pressure F_{BG} .
4. Compute material flux as follows: $F_{\text{Mg}} - F_{\text{BG}}$
5. Repeat steps (2) to (4) for all the cells except dopant cells. At the end of the flux measurements process close the main shutter and leave the Se cell open.

The flux ratio that is used to grow high quality ZnCdSe is $F_{\text{Cd}}/F_{\text{Zn}} = 2$ (Ref 30). The material fluxes that are typically used in this research for growing lattice match ZnCdSe

are as follows: $F_{\text{Zn}} = 1.0 \times 10^{-7}$ torr, $F_{\text{Cd}} = 2.0 \times 10^{-7}$ torr and $F_{\text{Se}} = 2.0 \times 10^{-6}$ torr.

Likewise to grow high quality lattice match ZnCdMgSe the $F_{\text{Cd}}/F_{\text{Zn}}$ ratio varied from 1.0 to 1.5 (Ref 30). Here the exact ratio will depend on the Mg flux and the growth temperature of the quaternary. In this research, a $F_{\text{Cd}}/F_{\text{Zn}} = 1$ was typically used for growing $\text{Zn}_{0.24}\text{Cd}_{0.18}\text{Mg}_{0.52}\text{Se}$ with a band gap of ~ 3.17 eV at 77 K. The material fluxes that were normally used are as follows: $F_{\text{Mg}} = 1.0 \times 10^{-7}$ torr, $F_{\text{Zn}} = 2.0 \times 10^{-7}$ torr, $F_{\text{Cd}} = 2.0 \times 10^{-7}$ torr, and $F_{\text{Se}} = 2.0 \times 10^{-6}$ torr. The group VI to group II ratio $F_{\text{Se}}/(F_{\text{Mg}} + F_{\text{Zn}} + F_{\text{Cd}})$ of ~ 4 should be maintained to ensure Se rich conditions for high quality II-VI growth.

To start the III-V growth, the sample/block is placed on the substrate heater of the III-V chamber. The temperature of the substrate is raised in 50° increments up to 250°C at which time the arsenic shutter is opened. During this deoxidation stage, the substrate temperature is raised in the following sequence: 250°C , 300°C , 330°C , 350°C and then in 10° increments until the oxide layer is lost. At this stage, the substrate surface is periodically monitored with the RHEED. In the initial stage of this deoxidation process, a diffuse ring which is characteristic of the amorphous oxide layer may be seen on the RHEED phosphor screen. On further heating of the substrate under arsenic flux, the diffuse ring is replaced with streaky line patterns that change during substrate rotation. During substrate deoxidation, the substrate is rotated until the 2-fold reconstruction can be identified. The substrate temperature is raised in increments of 10° until the 2-fold pattern changes to 4-fold. This change in the RHEED pattern indicates that all the surface oxide has been removed and we are at the point where phosphorous is being lost from the surface. On noticing this 2 x 4 transition, the substrate temperature is lowered by 30° to

prevent further loss of phosphorus which could damage the substrate surface. This deoxidation process is followed by the deposition of 0.25 μm buffer layer of InGaAs that is lattice matched to InP. During the growth of the buffer layer, a 2×4 reconstruction pattern which is typical of an arsenic terminated InGaAs layer can be seen on the RHEED screen. This buffer layer ensures that a clean smooth layer is available for the growth of the II-VI epilayer(s). At the end of the InGaAs layer growth, the substrate is lowered to 250° C under arsenic flux. This step is critical because closure of the arsenic source at the growth temperature could result in a damaged epilayer. Loss of arsenic from the sample surface at the growth temperature could result in the formation of indium droplets which would render the sample unfit for II-VI epitaxial growth. Lowering the substrate down to 250° C before closing the arsenic source ensures the formation of an arsenic terminated surface. These steps are critical for the formation of a low defect density III-V/II-V interface during the II-VI growth. At the end of the III-V growth, the sample is transferred under vacuum to the front of the II-VI chamber.

The start of the II-VI growth process is initiated by placing the sample on the substrate holder of the II-VI chamber. The substrate temperature is raised to 200° C and then exposed to zinc flux for 40 seconds. Zinc irradiation is then followed by the growth of a 90 Å thick ZnCdSe buffer that is lattice matched to the InGaAs epilayer. The zinc irradiation step minimizes the formation of In_2Se_3 and Ga_2Se_3 complexes due to exposure of the III-V surface with background selenium. This step together with the growth of the low temperature ZnCdSe buffer layer has resulted in a lowering of the II-VI epilayer defect density to $\sim 10^4 \text{ cm}^{-3}$.³¹⁻³³ This low temperature treatment is followed by a five minute growth interruption during which the substrate temperature is raised under

selenium flux to 300°C. This is the optimal growth temperature for growing good quality ZnCdSe or ZnCdMgSe. At this time the necessary cell shutters are opened to commence growth of the desired II-VI epilayer. During this II-VI growth the epilayer is periodically monitored with the RHEED to determine the sample quality.

2.2.5 *In-situ* Monitoring of Growth Using RHEED

The Riber 2300P MBE chambers that were used for this research, is equipped with a RHEED system that enables *in-situ* monitoring of sample surface. During operation of the RHEED system, the RHEED gun produces an electron beam that strikes the substrate at a very small glancing angle ($\theta \sim 2^\circ$) (see Fig. 2.4).

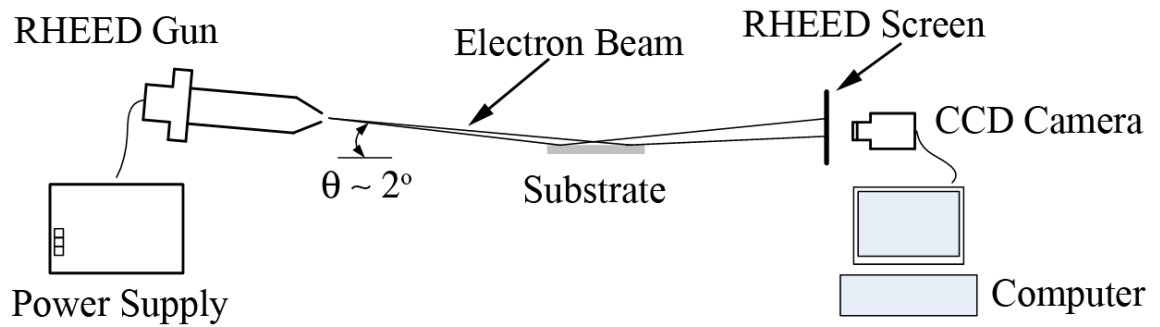


Figure 2.4: Description of the RHEED system used for *in situ* monitoring of material growth during the MBE process.

On striking the substrate, the stream of electron produces an image on a phosphor screen that is loaded with information about the substrates surface structure, chemistry, growth mode and growth rate. During the initial phase of MBE growth the RHEED gun produces

diffuse rings on the phosphor screen which is a characteristic of an amorphous structure (in this case an oxide layer on the substrate surface). In the presence of a crystalline epitaxial layer on the substrate surface, streaky line patterns that show azimuth dependence is produced on the screen. On monitoring the RHEED at a particular azimuth changes in the line pattern may be observed. This may be the result of changes in the lattice arrangement due to compositional changes in the epilayer. Also, on monitoring the RHEED pattern at a given azimuth, it is possible to detect oscillations in the pattern intensity as a result of changes in the substrate surface roughness during layer-by-layer growth (see Fig. 2.5). With this information it is possible to accurately determine the growth rate of the epilayer on the monolayer scale.

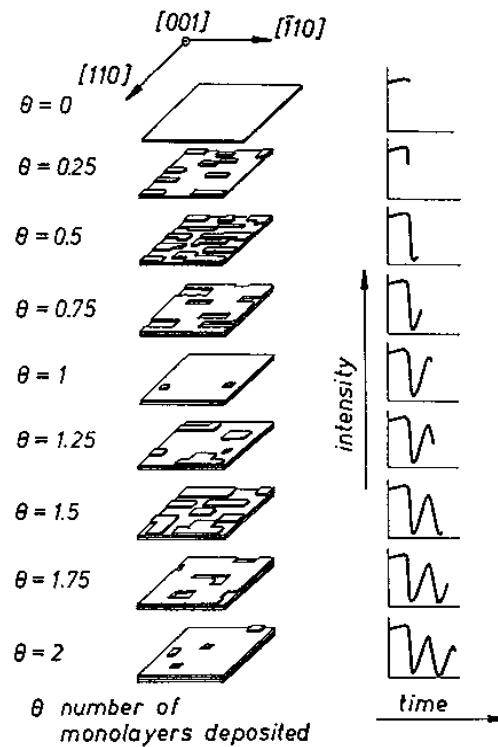


Figure 2.5: Diagram showing the relationship between surface roughness and RHEED intensity oscillations for epitaxial films grown using layer-by-layer growth mode.³⁴

2.3 Basics of the QC Lasers

2.3.1 Introduction

Lasers in general are composed of a gain medium, reflecting mirrors and/or a waveguide for containing light within the laser cavity. The QC laser is a semiconductor device with a Fabry Perot cavity in which the core or gain medium is composed of alternating periods of active/injector regions which are engineered to for emission at a desired wavelength and at the same time ensure population inversion at the lowest possible threshold condition (Fig. 2.6).

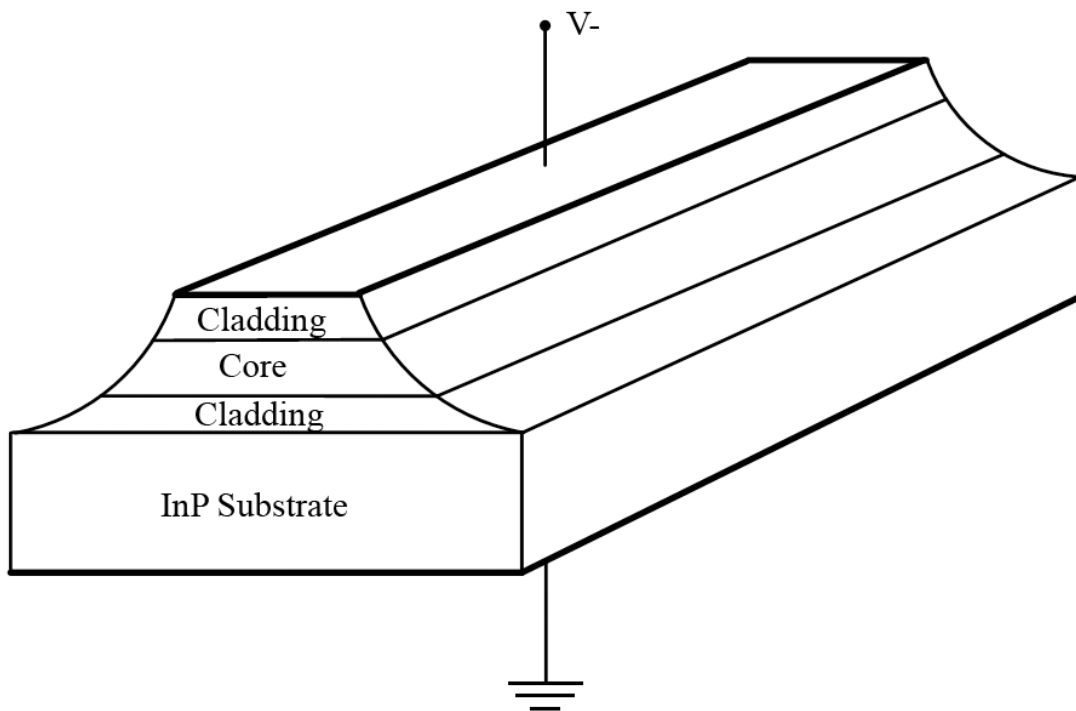


Figure 2.6: Schematic diagram of a QC laser showing waveguides, cladding and the core regions.

This semiconductor laser is also composed of a waveguide or cladding which serve the purpose of optically confining the emitted light within the laser core while minimizing

optical losses such as free carrier absorption. Generally, the performance of the QC laser degrades as the core temperature of the device increases. Hence, the thermal conductivity of the cladding material must be high enough to ensure very efficient heat dissipation from the laser core. Given that QC lasers are electrically pumped, the cladding must also be of high electrical conductivity to ensure high electron injection efficiency. The number of lasing modes that survive within the laser cavity is inversely proportional to the length of the laser cavity.³⁵ One way of ensuring single mode operation is to make the laser short enough to just confine one mode. For example, this means that for a laser with an effective refractive index of 3.6 and operating at 5 μm , the cavity length would have to be 0.7 μm . Using this strategy to produce single mode lasers would make device fabrication and packaging a very difficult undertaking, hence, alternative techniques must be employed to suppress undesired modes. To ensure single mode operation, the surface of the cladding is usually processed into a periodic grating (DFB QC lasers) which has the function of ensuring a single lasing mode survives.³⁶ The cleaved ends of the device act as the reflecting mirrors of the laser, hence, a good cleave is essential to ensure minimum optical loss at these reflecting surfaces. The optical losses of these mirrors can be modified using anti-reflection (AR) coatings.

2.3.2 Operating Principles of a QC Lasers

In the traditional semiconductor laser, light generation is usually the result of stimulated or spontaneous electron transition from conduction to valence band. As a result, the operating wavelength is dictated by the semiconductor bandgap. Given the fact that the inter-band emission wavelength of semiconductor materials is usually in the

visible to near IR range, the quantum cascade design as proposed by Kazarinov and Suits¹ is the only viable option for realizing mid-IR semiconductor lasers. The QC laser is a unipolar device in which only the conduction or valence band is involved during the device operation. For some material systems such as the II-VIs where p-type doping is a challenge, QC laser production is still possible since the conduction band can be used. Unlike other semiconductor lasers (diode, QW laser) the QC laser depends on intersubband (IS) transitions as depicted in Fig. 2.7.

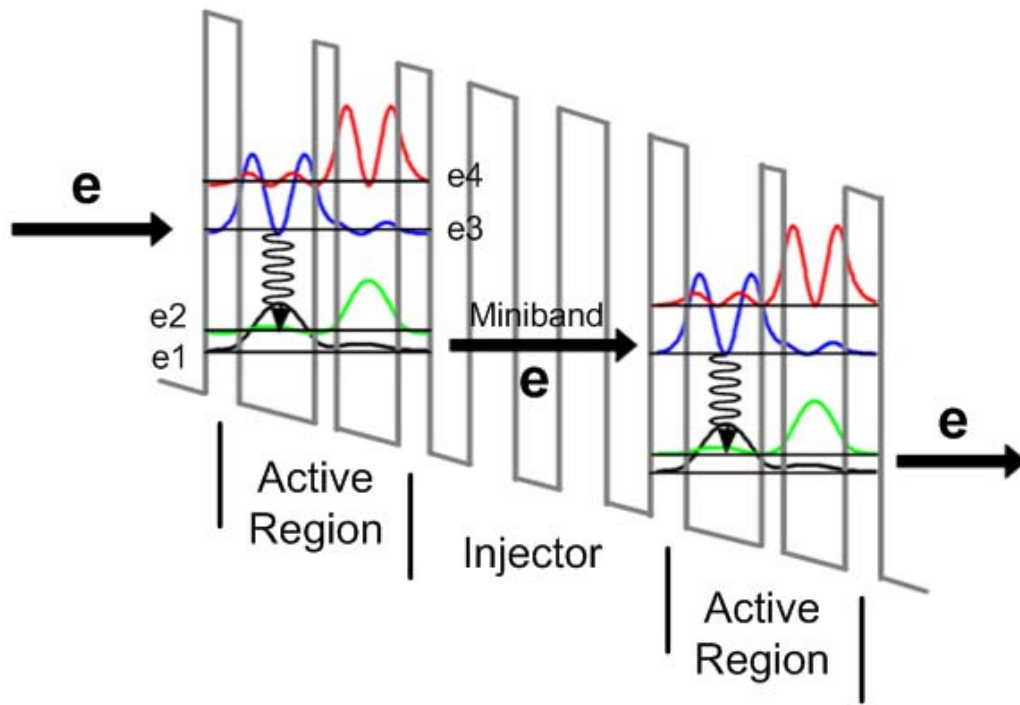


Figure 2.7: Illustration of light generation in a QC laser structure. In this scheme the potential exist for one injected electron to generate an electron in each active region.

Hence the internal quantum efficiency of the laser could be in excess of 100 %.

In these devices, the operating wavelength can be easily tuned by varying the thickness of the quantum well in the active region of the device. Here the operating wavelength is limited by the dept of the quantum wells (CBO) and mid-IR operation is possible. The

fact that the quantized energy levels of the conduction band are atomic in nature and are of the same curvature, the joint density of states of the lasing energy levels of the QC laser is very sharp.³⁷

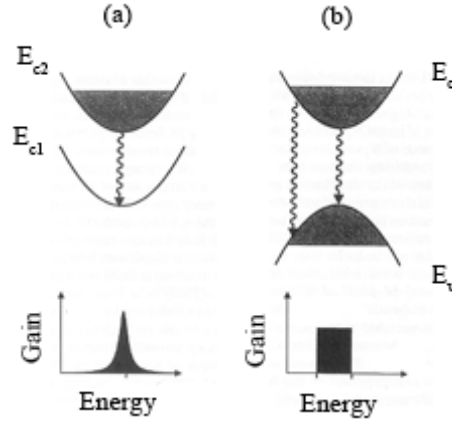


Figure 2.8: Comparison between the gain linewidths of (a) intersubband and (b) interband devices.³⁷

This result in gain linewidths with very narrow full width at half maximum (FWHM) and broadens mainly due to electron phonon interactions. On the other hand, as depicted in Fig. 2.8, the curvature of the lasing energy levels of interband semiconductor lasers is very different resulting in a joint density of states and gain linewidth FWHM that is significantly broader. The overall gain of the interband laser saturates as the quasi-Fermi levels move into the conduction and valence band respectively. In the case of the IS lasers, such limitation does not exist. The gain is directly related to the amount of electrons that can be pumped into the upper lasing state of the active region and the number of active/injector periods, N_p , within the device core ($G = G_p N_p \Gamma_p$ where G_p : gain per lasing stage, N_p : number of lasing stages, Γ_p : waveguide confinement factor).

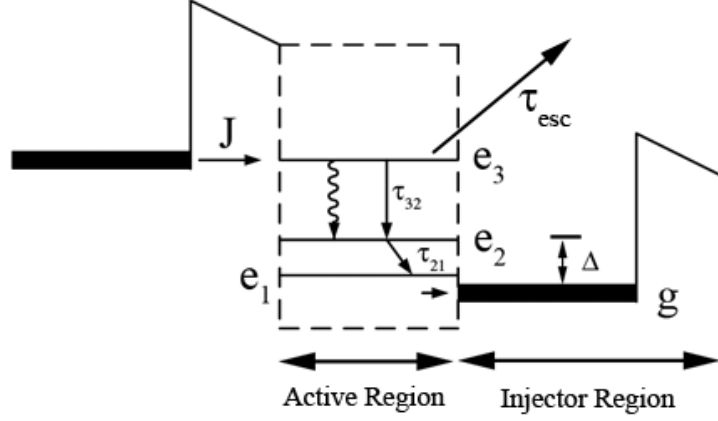


Figure 2.9: Schematic diagram of a QC laser active/injector region. Straight arrows show non-radiative relaxation while the spiral arrow shows radiative optical emission.

The schematic diagram of an active/injector period of a generalized QC laser is shown in Fig. 2.9. In this three level system, the primary role of the injector region is to channel electrons to the upper lasing level, e_3 , and quickly extract them from the active region of the QC laser via e_1 . J represents the electron density entering the QC laser while J_3 represents the electron density in e_3 . τ_3 and τ_2 represents the nonradiative lifetime of electrons with the e_3 and e_2 energy levels respectively:

$$\tau_3 = \left(\frac{1}{\tau_{ph}} + \frac{1}{\tau_{esc}} \right)^{-1} \quad (2.1)$$

$$\tau_2 = \left(\frac{1}{\tau_{21}} + \frac{1}{\tau_{2g}} \right)^{-1} \quad (2.2)$$

where $1/\tau_{ph}$ and $1/\tau_{esc}$ is the rate at which electrons are lost from e_3 through phonon relaxation and escape to the continuum respectively. Also $1/\tau_{21}$ is the rate of electron lost for e_2 to e_1 due to electron-phonon interactions while $1/\tau_{2g}$ represents the rate at which electrons is lost to the graded injector as a result of phonon relaxation. The injection

efficiency, which is the ratio of the electron density in the injection region to that in $\mathbf{e}_3$, is calculated as follows:

$$\eta_i = \frac{\mathbf{J}_3}{\mathbf{J}} \quad (2.3)$$

The electron densities in the lasing states of the QC laser, $\mathbf{n}_3$ and $\mathbf{n}_2$ can be expressed as follows:

$$\mathbf{n}_3 = \frac{\eta_i \mathbf{J}}{q} \tau_3 \quad (2.4)$$

$$\mathbf{n}_2 = \mathbf{n}_3 \frac{\tau_2}{\tau_{32}} \quad (2.5)$$

where τ_{32}^{-1} is the rate at which electrons decay nonradiatively from $\mathbf{e}_3$ to $\mathbf{e}_2$ and q is the charge of an electron. In the absence of light radiation, the necessary condition for population inversion is satisfied when the following is true:

$$\mathbf{n}_3 - \mathbf{n}_2 = \frac{\eta_i \mathbf{J}}{q} \tau_3 \left(1 - \frac{\tau_2}{\tau_{32}} \right) \succ 0 \quad (2.6)$$

From (2.6) it can be interpreted that $\tau_{32} \succ \tau_2$ is a necessary condition for population inversion. In the event that $\tau_3 = \tau_{32}$ (which is equivalent to saying the rate of electrons entering $\mathbf{e}_2$ is equal to the rate at which they leave $\mathbf{e}_3$), equation (2.6) can be rewritten as follows:

$$\mathbf{n}_3 - \mathbf{n}_2 = \frac{\eta_i \mathbf{J}}{q} (\tau_3 - \tau_2) \quad (2.7)$$

From (2.6) and (2.7) the critical importance of keeping τ_2 to a minimum can be seen. To attain this objective, the active regions of QC lasers are designed such that there is LO phonon resonance between $\mathbf{e}_2$ to $\mathbf{e}_1$ (This has the effect of maximizing $1/\tau_{21}$).

2.3.2.1 Rate Equations and Optical Gain

In the presence of optical emission, the rate equations for the QC laser are given as follows (Ref. 38):

$$\frac{d\mathbf{n}_3}{dt} = \frac{\mathbf{J}}{e} - \frac{\mathbf{n}_3}{\tau_3} - S g_c (\mathbf{n}_3 - \mathbf{n}_2) \quad (2.8)$$

$$\frac{d\mathbf{n}_2}{dt} = \frac{\mathbf{n}_3}{\tau_{32}} + S (\mathbf{n}_3 - \mathbf{n}_2) - \frac{\mathbf{n}_2}{\tau_2} + \frac{\mathbf{n}_g \exp(-\Delta / kT)}{\tau_2} \quad (2.9)$$

$$\frac{dS}{dt} = \frac{c}{n} \left\{ [g_c (\mathbf{n}_3 - \mathbf{n}_2) - \alpha] S + \beta \frac{\mathbf{n}_3}{\tau_{sp}} \right\} \quad (2.10)$$

Note: S : the photon flux density g_c : gain coefficient τ_{sp} : spontaneous emission time
 $\mathbf{n}_g$: electron density in the injector region α : is the total optical loss (wave guide plus mirror losses)
 β : contribution of spontaneous emission optical emission to lasing mode(s)

The thermal contribution to $\mathbf{n}_2$ as seen in (2.9) is $\mathbf{n}_2^{therm} = \mathbf{n}_g \exp(-\Delta / kT)$. With $\mathbf{n}_g \gg \mathbf{n}_2$ and $\mathbf{n}_3$, an increase in operating temperature could result in a significant backflow of electrons from the injector to $\mathbf{n}_2$ (thermal backfilling). Two figures of merit for a QC laser are the threshold current (the minimum current required for lasing) and the gain. Under steady state operation of the QC laser (where $d\mathbf{n}_3/dt = d\mathbf{n}_2/dt = dS/dt = 0$), if one assumes that the contribution for spontaneous emission is negligible, the threshold current density for the laser can be expressed as follows:

$$\mathbf{J}_{th} = q \frac{1}{\tau_3} \frac{(\alpha / g_c + \mathbf{n}_2^{therm})}{1 - \tau_2 / \tau_{32}} \quad (2.11)$$

On the other hand, the peak optical gain per active region of the QC laser is also expressed as (Ref. 39):

$$\mathbf{G}_p = \frac{4\pi q^2}{\epsilon_0 n \lambda} \frac{z_{23}^2}{2\gamma_{23} L_p} (\mathbf{n}_3 - \mathbf{n}_2) \quad (2.12)$$

From equations (2.9), (2.11) and (2.12) it is clear that thermal backfilling could result in an increase in the device threshold current and a reduction in overall gain. To improve the high temperature performance of the QC laser $\mathbf{n}_2^{therm}$ must be minimized. To this end, steps must be taken to design a QC laser with as large an energy difference between $\mathbf{e}_2$ and $\mathbf{g}$ (ground state of the injector) as possible.

2.3.2.2 Active/injector Region Design

To ensure production of a high performance QC lasers at room temperature and above, the active region must be designed to minimize nonradiative loss of electron from $\mathbf{e}_3$ due to electron-phonon interaction and loss to the continuum (which is the same as saying τ_3 must be very large).

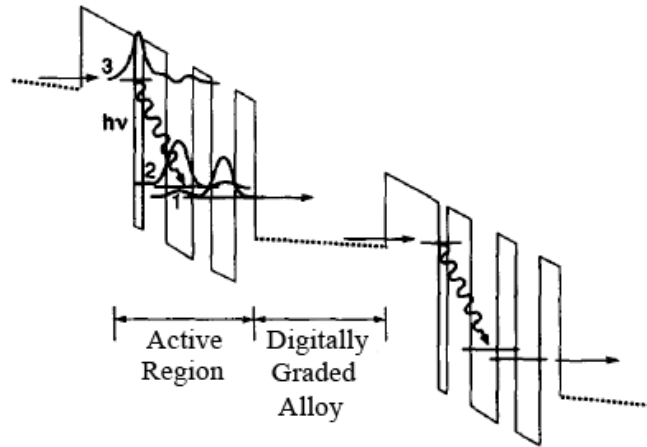


Figure 2.10: QC laser with diagonal transition active regions.⁴⁰

Also, the rate of electron loss from e_2 must be maximized (very small τ_2). To date, active regions designs are of two types. In the first design as is shown in Fig. 2.10, electronic transitions between the lasing states e_3 and e_2 occurs across a barrier (diagonal transition).

In the second design, as shown in Fig. 2.11, the lasing state transitions takes place within the same quantum well and hence no barrier is crossed in the process (vertical transition).^{40,41} The first design has the advantage of high electron injection efficiency and fairly large τ_3 values. This advantage is offset by a reduction in gain due to linewidth broadening which is induced by electronic interaction with rough well/barrier interfaces.

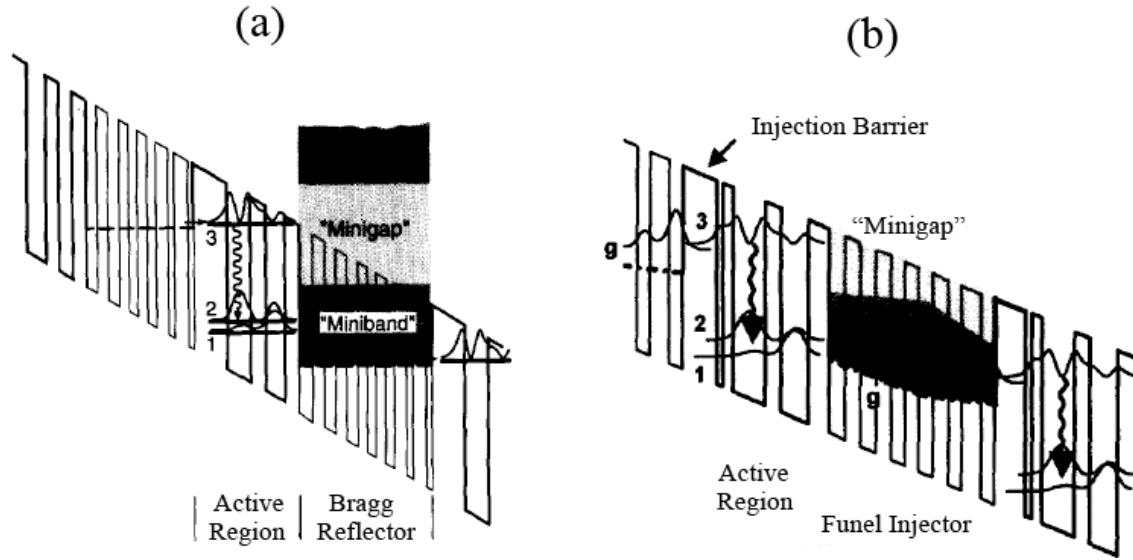


Figure 2.11: QC lasers with vertical transition active regions: (a) the injector is designed with a chirped superlattice while in (b) the funnel injector is presented.⁴⁰

In the second design (vertical transition) (Fig. 11), the resulting QC lasers are less sensitive to interface roughness. In this design the e_2 and e_1 energy separation is resonant to LO phonons hence, the lifetime of electrons in e_2 , τ_2 , is dramatically reduced. As a consequence, QC lasers with this design have much smaller linewidths and larger optical

gain than their diagonal counterparts. The injector regions of QC lasers with the second design are usually chirped or funnel shaped superlattices. In both cases the superlattice serves as a Bragg reflector reducing the loss of electrons into the continuum and as a means of increasing the energy spacing, Δ , between the ground level in the injector and e_2 .

The use of the chirped superlattice in the injector region enables the QC laser designer to increase Δ by increasing the number of wells/barriers. As the number of well/barrier pairs in the injector increases, the performance of the device eventually peaks and degrades. This decline in performance is due to the following:

- (a) The number of gain regions per unit length decreases and so does the overall laser gain.
- (b) The overall resistance across the laser increases. This results in the need for a higher bias voltage. Consequently the QC laser heats up and there is an increase loss of electrons from e_3 and the problem of thermal backfilling becomes much more significant.

To overcome problems (a) and (b), the chirped superlattice injector was replaced by one that is funnel shaped.⁴⁰ The funnel shaped injector design enables the wave function in the injector to converge in the vicinity of the active region. Apart from increasing the injection efficiency of electrons into the active region, this design results in the funneling electrons into the ground state of the injector and increasing Δ with a shorter injector. The fact that Δ can be increased with a shorter injector, the doping level of the injector can be kept to a minimum. Also, this design enables Δ to be increased without reducing the

number of gain stages per device epilayer thickness. Overall, the funnel shaped injector enables the production of QC laser with very promising high temperature performance.

2.3.2.3 Waveguide

The lasing threshold of all lasers is reached when the cavity loss is equal to the laser gain. Therefore in order to ensure lasing, steps must be taken to increase the gain of the device. One of the parameters that affect the gain of the QC laser is Γ , which is a measure of the amount of light that is confined in the laser core. Given that the laser gain as described in (2.13) is directly proportional to Γ , every effort must be made to incorporate a waveguide that will provide a large confinement factor without contributing to an increase in the cavity losses and resistance to current flow.

$$G_{QCL} = \left(\frac{4\pi q^2}{\epsilon_0 n \lambda} \frac{z_{23}^2}{2\gamma_{23} L_p} \right) \times \left(\frac{\eta_i J}{q} (\tau_3 - \tau_2) \right) N\Gamma \quad (2.13)$$

Light confinement in most QC lasers is achieved using a planar waveguide as described in Fig. 2.12. The confinement factor Γ , for such a guide can be expressed as

$$\Gamma = \frac{\int_{-d/2}^{d/2} E_y^2(y) dy}{\int_{-\infty}^{\infty} E_y^2(y) dy} \quad (2.14)$$

where $E_y(y) = A \cot \theta_m \cos(ky) + B \cot \theta_m \sin(ky)$ with $k = nk_0 \sin \theta_m$.⁴²

θ_m are the bounce angles corresponding to transverse mode that are supported by the waveguide and laser cavity. These bounce angles are determined from the solution of the transcendental equation

$$\tan\left(k \sin \theta - m \frac{\pi}{2}\right) = \frac{n_1}{n_2^2 \cos \theta} \sqrt{n_1^2 \sin^2 \theta - n_2^2} \quad (2.15)$$

An expression for the light the escape the laser core can be obtained by solving the Helmholtz equation

$$\left(\Delta^2 + n_2^2 k_0^2\right) E_{y,ext}(y, z) = 0 \quad (2.16)$$

where $E_{y,ext}(y, z) = E_y(y) \exp(-jB_m z)$ for $y = \pm d/2$.

From the solution of (2.16), the decay rate or extinction coefficient of the escaped light was determined be

$$\frac{\partial^2}{\partial y^2} E_y(y, z) - \gamma_m E_y(y, z) = 0 \text{ where } \gamma_m = k_0^2 (n_1^2 \cos^2 \theta_m - n_2^2) \quad (17)$$

The amount of light that eventually leak into the cladding layers can be described by the following equations:

$$\begin{cases} A \exp(-\gamma_m y), & y \succ d/2 \\ A \exp(\gamma_m y), & y \succ -d/2 \end{cases} \quad (18)$$

Here the decay rate or extinction coefficient λ_m determines the penetration depth of light into the cladding. The larger the difference between the square of the modulated core index ($n_1^2 \cos^2 \theta_m$) and that of the cladding (n_2^2), the shorter the penetration depth of light into the cladding. Hence to ensure light confinement a thick cladding layer would not be necessary. This is important since in the opposite case where a thick cladding would be required, the confinement factor as described by (2.14) would be much reduced.

Furthermore, a thick cladding could result in increase optical losses (such as free carrier absorption) and poor heat extraction for the laser core. These drawbacks could result in a reduction in the laser gain and an increase in the lasing threshold of the QC device.

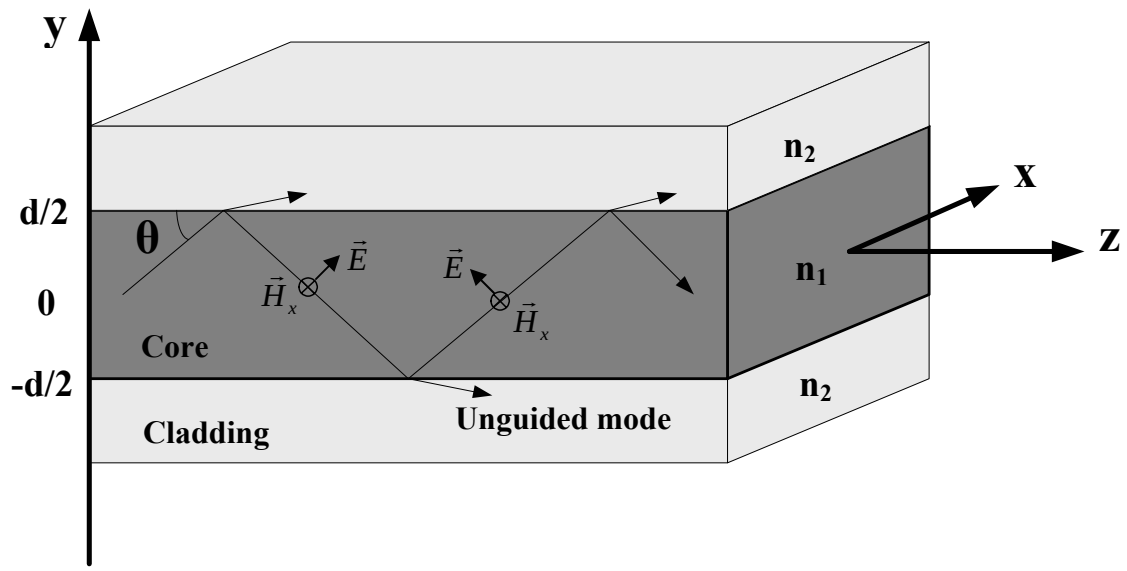


Figure 2.12: Description of QC laser waveguide. Here the refractive index of the core and cladding are n_1 and n_2 respectively, while the core thickness is d .

Chapter 3

Characterization of Thin Film Semiconductor Materials

In this chapter the characterization techniques that were used to analyze samples throughout this research will be discussed. The experimental setup and operation principles of x-ray diffraction (XRD), photoluminescence (PL), Hall effect and contactless electro-reflectance (CER) analysis of epitaxially grown semiconductor material will also be presented. Additionally, scanning electron microscopy (SEM) and Fourier transform infra-red microscopy were two very important research tools that were used in this work. Therefore, these characterization techniques will also be discussed.

3.1 X-Ray Diffraction

X-ray diffraction (XRD) is a characterization technique that is frequently used by researchers in the semiconductor industry, especially semiconductor crystal growers. This technique is a powerful tool that can be used to determine the lattice constant of the grown epilayer. Lattice constant determination is critically important since this information can be used to determine the lattice mismatch between the epilayer and the substrate. This in turn could be used to evaluate the epilayer strain. Furthermore, with this knowledge, the composition of bulk semiconductor materials and the periodicity and interface quality of multi-quantum well structures can be deduced. In this section the fundamental principles of XRD semiconductor analysis will be discussed. Details will be

given on the use of single crystal XRD and double crystal XRD characterization methods. Also, a description of the XRD system used in this research will be presented.

3.1.1 X-ray Diffraction Fundamentals

X-rays used in most laboratory equipment are produced when high energy electrons are forced to impinge onto a metallic target. Generally, the x-ray tube is evacuated to prevent electron scattering. This tube is comprised of a cathode, an anode and beryllium windows that are placed in the vicinity of the anode to facilitate the escape of x-ray photons. During the operation of the x-ray system, a significant amount of heat is produced as the electrons crash into the target metal or anode. Therefore, in order to ensure efficient heat extraction, the target metal of choice is usually copper because of its high thermal conductance. The anode is usually cooled with a close loop water cooling system. Electrons are generated in the tube by applying current to the cathode. The electrons that escape from the heated cathode are accelerated to the anode or target metal using an applied voltage of about 30 KV as described in Fig. 3.1.

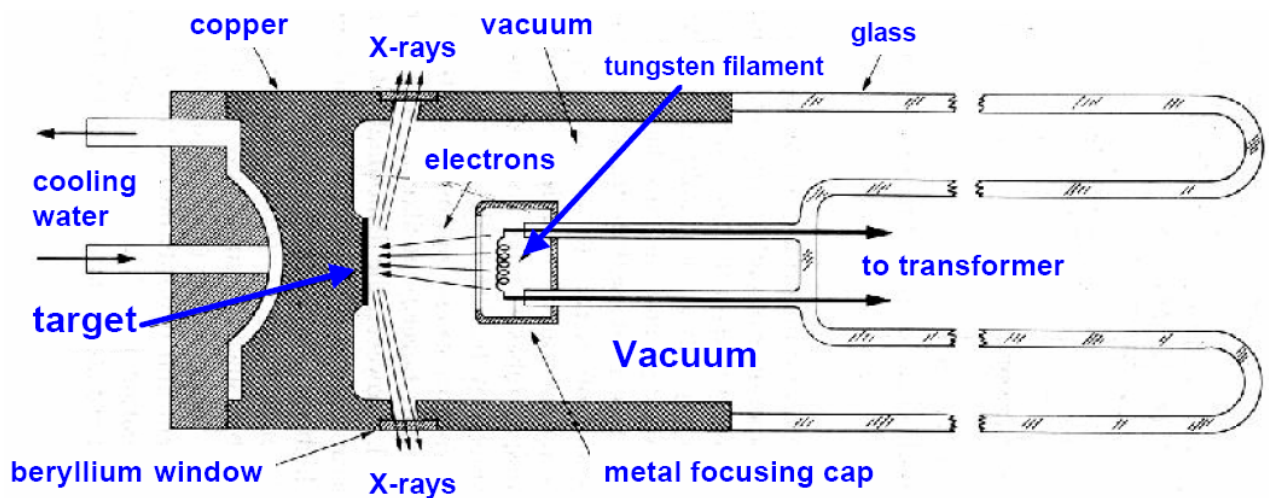


Figure 3.1: Cross-section of the x-ray tube used in the Rigaku x-ray generation system.⁴³

Before encountering the anode, the electrons typically gain an energy of about 30 KeV. As these electrons crash into the target, x-ray photons with a continuum of energies as described by Fig. 3.2 are produced. This continuous emission is called the Bremsstrohlung radiation. In some cases the collision would result in the removal of atomic electrons from the inner electronic levels such as the K, L and M electron shells. X-rays are also released when electronic transitions take place between these inner shells. K_{α} radiation occurs when $L \rightarrow K$ electronic relaxation occurs. The $K_{\alpha 1}$ and $K_{\alpha 2}$ x-ray lines are due to $L_{3(2p_{3/2})} \rightarrow K_{1s}$ and $L_{2(2p_{1/2})} \rightarrow K_{1s}$, respectively as depicted in Fig. 3.3. These characteristic x-ray lines are typically used to identify elements in x-ray topography studies. For copper, the emission wavelength corresponding to this radiation is about $1.52 \mu\text{m}$ which is on the order of the interplanar distance of most materials. Furthermore, the high intensity of the $\text{Cu}K_{\alpha 1}$ characteristic line makes it very suitable for studying the properties of semiconductor materials.

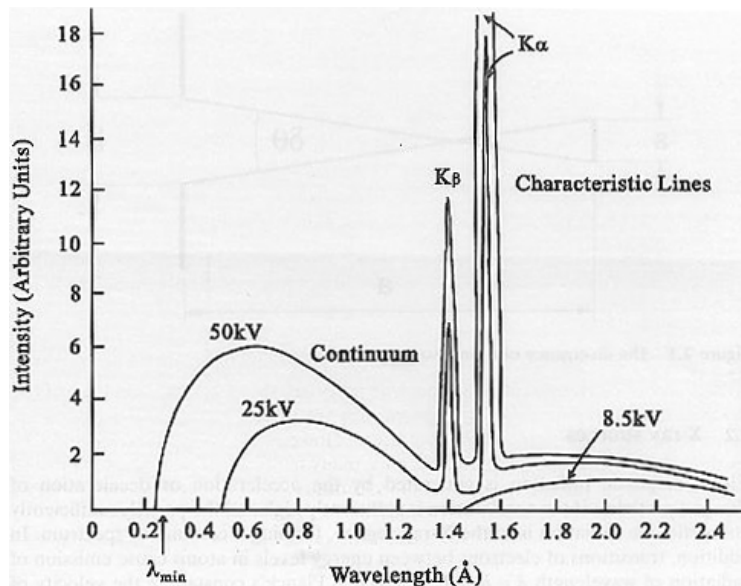


Figure 3.2: Emission spectra for an x-ray tube with a copper target.⁴⁴

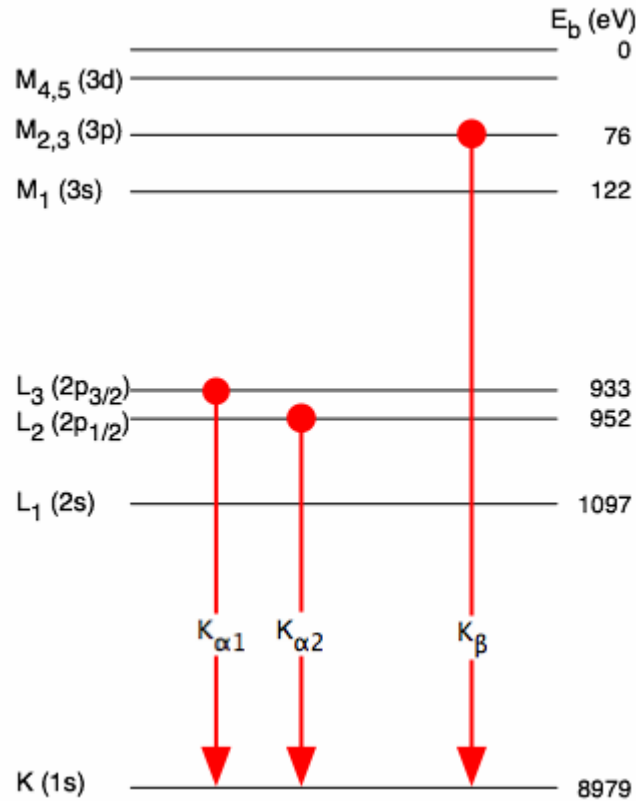


Figure 3.3: Diagram showing the electronic transitions corresponding to the CuK_{α} and CuK_{β} x-ray emission lines.⁴⁵

3.1.2 High Resolution X- Ray

The x-ray equipment that is used to characterize semiconductor samples contains an x-ray source that directs the photon flux at a glancing angle as described in Fig. 3.4. During the x-ray analysis, the detector is scanned in the path of the reflected light from the various crystal planes of the semiconductor sample. The reflected light from these planes interacts to produce a diffraction pattern the gives insight into the inter-atomic spacing of the sample. The amount of information that can be resolved from the x-ray scan depends on how well the impinging radiation approximates the theoretical plane

wave (or how collimated is the beam).

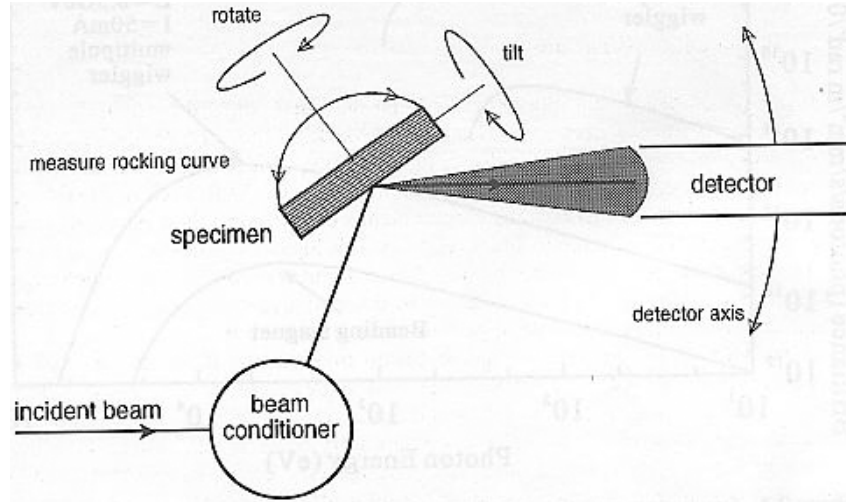


Figure 3.4: Schematic representation of high resolution x-ray system.⁴⁶

In the single axis x-ray system the beam divergence $\delta\theta$, is a function of the size of the x-ray source h , the slit size s and the sample distance from the source a .

$$\delta\theta = \frac{h + s}{a} \quad (3.1)$$

In order to reduce the beam divergence in this system to closely approximate the plane wave, a large a , or sample/source separation is required. Generally, the radiation intensity drops off with distance. Therefore, this approach of beam collimation would be defeated by the poor signal to noise ratio that arises due to the reduced x-ray intensity. The high resolution x-ray diffraction systems that are used in most laboratories are produced using beam conditioners to reduce the divergence angle of the incident radiation. In some instances, XRD studies are done using the highly collimated synchrotron light source.

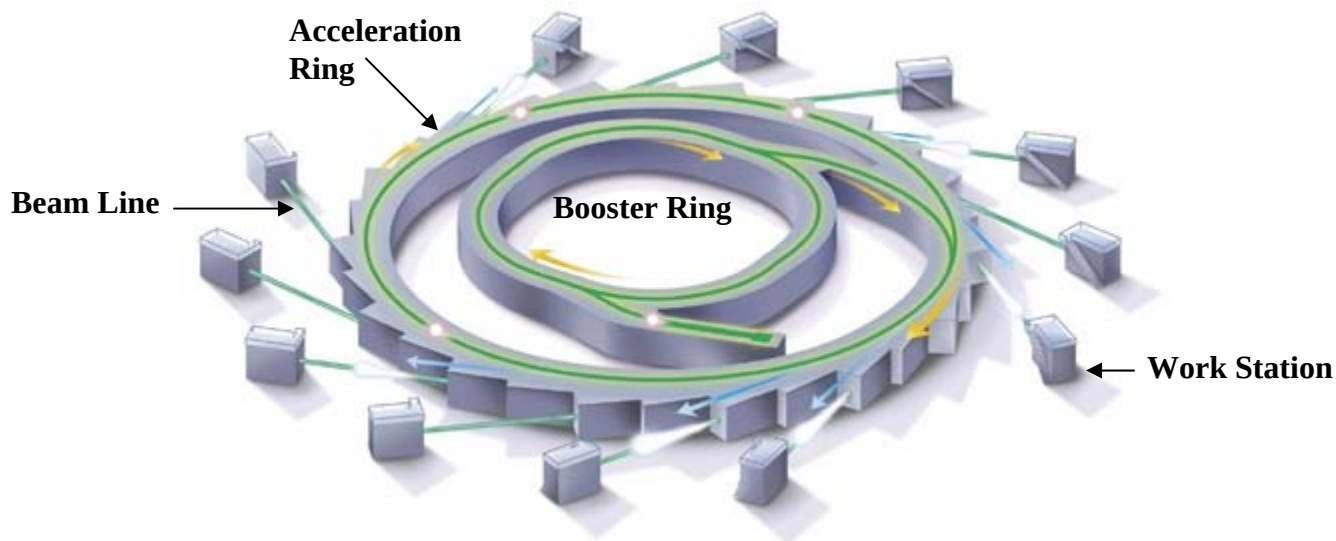


Figure 3.5: Schematic diagram of the synchrotron used for HRXRD generation.⁴⁷

The synchrotron is usually in the shape of a polygon with rounded edges and could cover several acres of land. This high vacuum tubular structure contains a central loop of magnets that is responsible for bending the electron beam. As the electrons accelerate to speeds close to that of light, a highly collimated continuum of x-ray beams are produced (see Fig. 3.5). This light source is ideal for studying semiconductor structures because besides being highly collimated, the intensity is several orders of magnitude higher than that of the regular laboratory high resolution x-ray system. This allows the resolution of most of the details in a crystalline semiconductor structure.

In this research, both the single axis and synchrotron systems were used. A description of the single axis single crystal XRD (SCXRD) Rigaku system and a Blake Industries double crystal XRD (DCXRD) system are shown side by side in Fig. 3.6

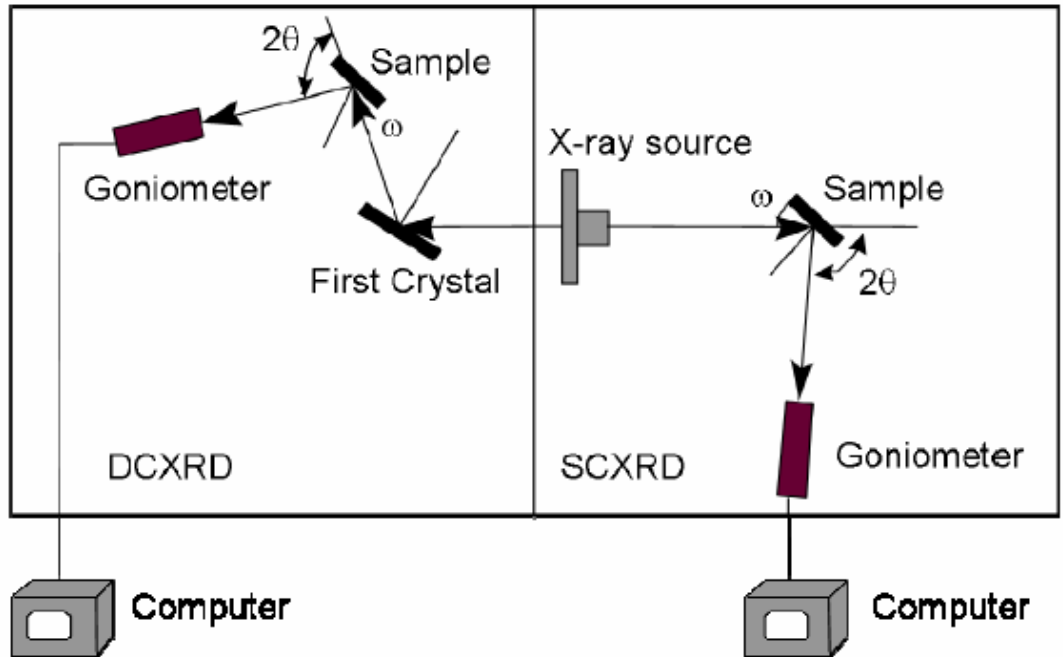


Figure 3.6: Illustration of the single axis XRD systems used for studying thin film semiconductor material.

After growing the semiconductor structure, the sample is first evaluated with the SCXRD system in order to make a determination of the lattice mismatch.

The XRD systems described in Fig. 3.6 are comprised of a detector (goniometer) that is attached to an outer wheel which scans an angle of (2θ). The substrate, on the other hand, can be attached to the inner wheel that scans an angle θ or half that of the detector during a coupled scan. In the SCXRD system the only crystal that interacts with the x-ray is the semiconductor sample. During the DCXRD system rocking curve measurement, the x-ray is first passed through a (001) germanium (Ge) crystal which filters out the low intensity $\text{CuK}\alpha_2$ line and makes the source light highly monochromatic.

The samples that were studied in this research were grown on (001) plane indium phosphide (InP) substrates. For these sample the highest intensity diffraction peak was

observed at an angle $2\theta = 63.1^\circ$. Therefore, this Bragg angle which corresponds to the (004) crystal plane was used for all XRD studies. After the growth of a new batch of samples, the SCXRD system was first used to obtain an estimate of the lattice mismatch between the substrate and the epilayer. First, the sample was attached to the inner wheel (θ) of the XRD system while the detector was placed at the Bragg angle. With the x-ray on, a rough scan was performed to obtain proper sample alignment with the detector. During this alignment step the detector was kept at the Bragg angle and the sample was made to rotate about 5° . At the end of the scan the sample was brought to the position corresponding to the peak of the detector signal intensity. This position is then set to 31.33° which is half that of the detector. On completion of this alignment a coupled scan is performed using the MDI control software. The resulting x-ray scan contains a pair of peaks ($\text{CuK}_{\alpha 1}$ and $\text{CuK}_{\alpha 2}$ separated by $2\theta \sim 18^\circ$) corresponding to the substrate and the epilayer, respectively (see Fig. 3.7). The $\text{CuK}_{\alpha 1}$ peak usually has an intensity that is twice that of $\text{CuK}_{\alpha 2}$.

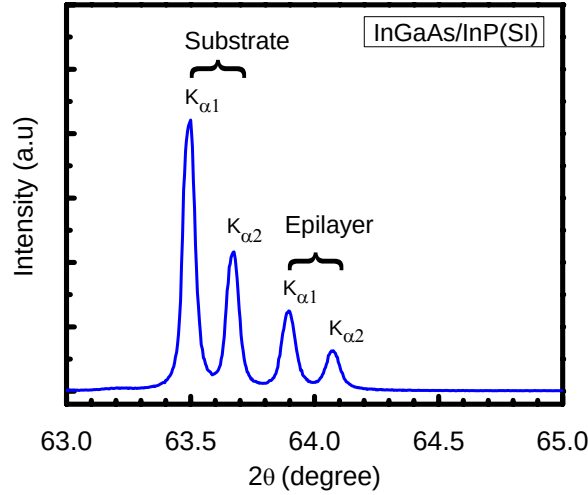


Figure 3.7: SCXRD curve for bulk InGaAs grown on InP semi-insulating substrate.

The $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks can be seen for epilayer and substrate.

In instances where the lattice mismatch was small and there was an overlap between the substrate and epilayer peak, the DCXRD system was used. The DCXRD rocking curve measurement was also performed to get a more accurate measure of the lattice mismatch and lattice constant. The DCXRD scan was performed in a manner similar to that of the SCXRD measurement. Here the alignment was done manually with the use of the goniometer (detector) that was kept at the Bragg angle during scans.

3.1.3 Analysis of Thin Films

Bragg was one of the early pioneers that set the theoretical foundation for the study of crystal structures with x-rays. Bragg's law and its relationship to XRD analysis is schematically illustrated in Fig. 3.8.

$$n\lambda = 2d \sin\theta_B \quad (3.2)$$

Here λ represents the wavelength of the incident x-ray radiation. The value of the x-ray wavelength used throughout this work was $\lambda=1.5406 \text{ }\mu\text{m}$. θ_B represents incident angles that gave rise to interference peaks when XRD analysis was performed on the substrate material. The various θ_B values that were observed correspond to planes parallel to crystal planes. The XRD analysis that were frequently performed throughout this research used $\theta_B = 31.33^\circ$ relating to the (004) substrate since this incident angle gave rise to interference peaks with maximum intensity. Finally, $d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ corresponds to the crystal plane spacing with Miller indices (hkl) and a representing the substrate lattice constant.⁴⁸

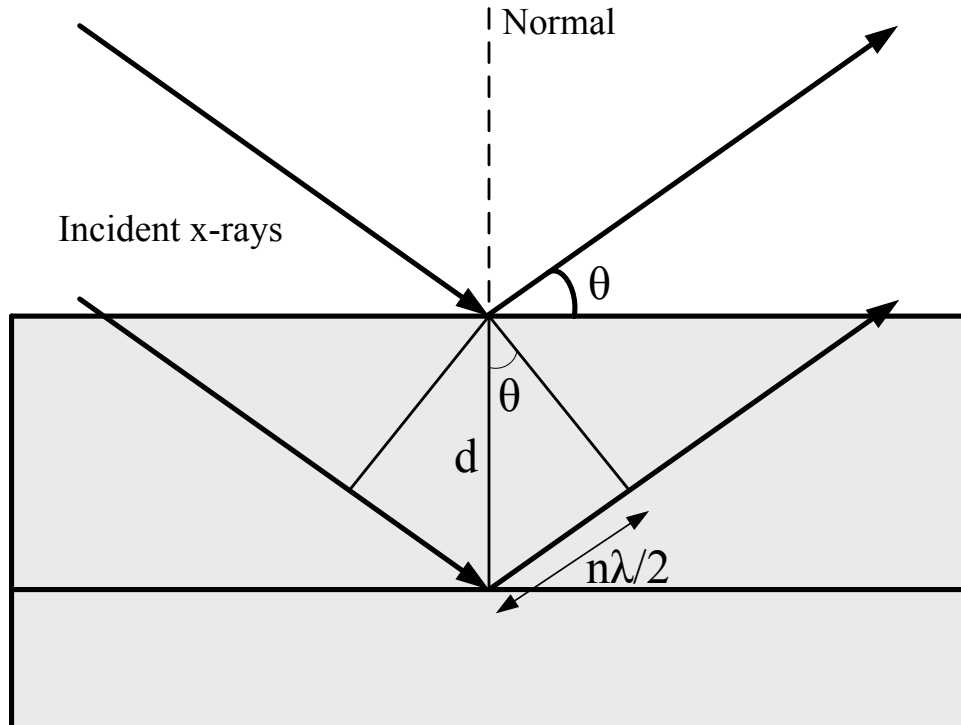


Figure 3.8: Description of path taken by x-ray photons during (004) XRD scan. This plot was used for deriving the Bragg equation.

3.1.3.1 Calculation of Bulk Layer Lattice Constant

The MBE growth of semiconductor material on a given substrate usually results in an epitaxial layer that may be lattice matched, pseudomorphic or fully strained, and partially or fully relaxed. These conditions are illustrated in Fig. 3.9.

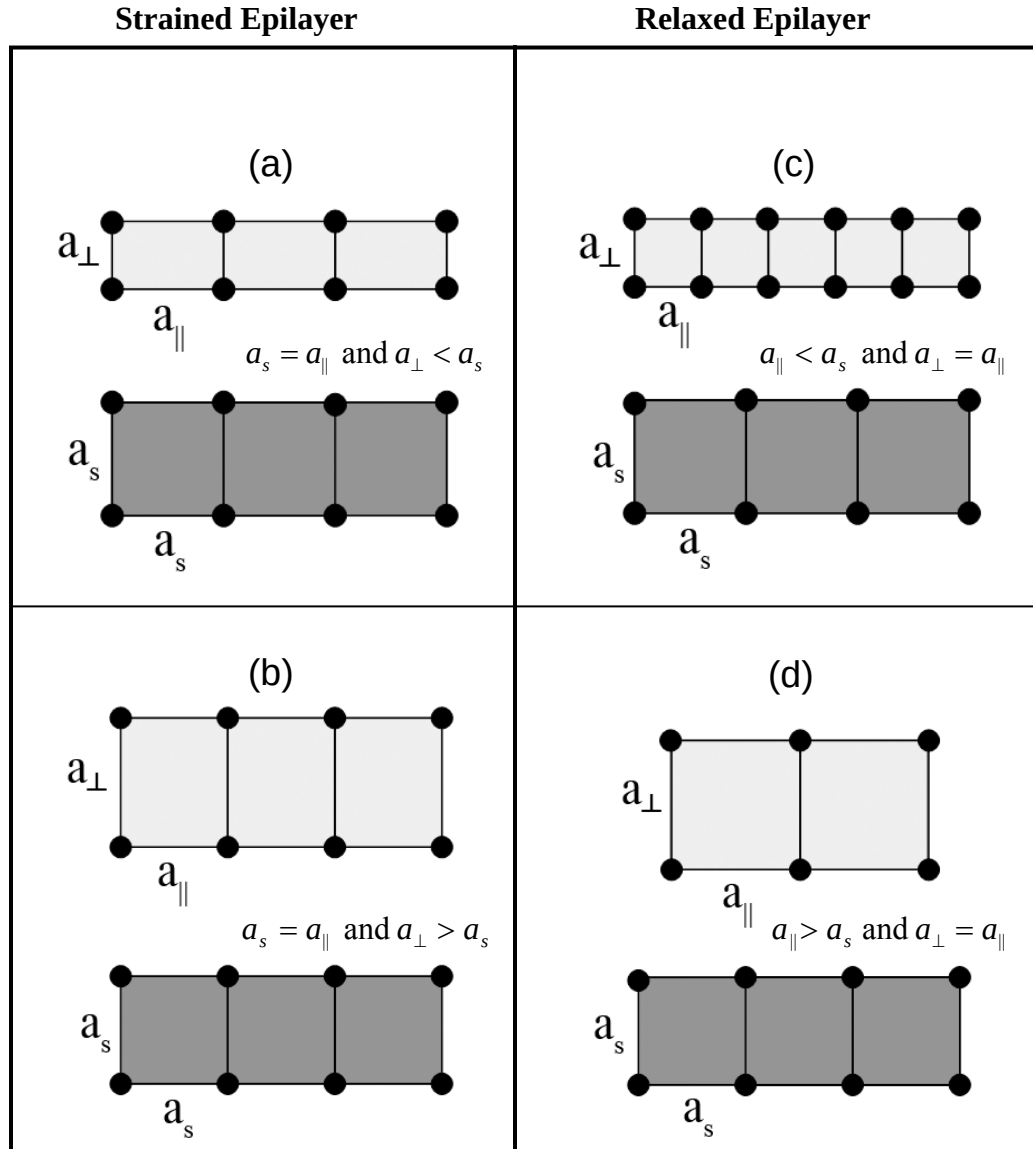


Figure 3.9: Arrangement of atoms in strained and relaxed epitaxial films. (a) and (b) illustrate the effects of tensile and compressive strain, respectively. (c) and (d) show the atomic arrangement when complete relaxation is achieved.

The parallel lattice constant $a_{\parallel}$ of pseudomorphic (strained) epitaxial films are identical to that of the substrate a_s on which the film is grown. The perpendicular lattice $a_{\perp}$ constant, on the other hand, is different due to tensile or compressive strain. On increasing the thickness of the epitaxial film there is a steady buildup of compressive or tensile strain. This distortion eventually reaches a critical point at which lattice relaxation commences. For cubic materials, when the film is completely relaxed, the film's perpendicular and parallel lattice constants are equal in value ($a_{\parallel} = a_{\perp}$). In the intermediates stage when $a_{\parallel} \neq a_s$, both $a_{\perp}$ and a_s have to be determined in order to calculate the epitaxial film lattice constant a_L . Regardless of the degree of strain in the epilayer, the lattice mismatch and lattice constant can be evaluated by making use of the Bragg formula and the Poisson parameter ν which is defined as the ratio of the parallel and perpendicular strain of the crystalline structure.^{49,50}

$$\nu = -\frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} \quad (3.3)$$

The epilayer lattice constant is computed as follows:

$$a_L = a_{\perp} \left(\frac{1-\nu}{1+\nu} \right) + a_{\parallel} \left(\frac{2\nu}{1+\nu} \right) \quad (3.4)$$

Using equation (3.3) and (3.4) the lattice mismatch can be computed as shown in (3.5):

$$\Delta a = \frac{a_L - a_s}{a_s} \quad (3.5)$$

In this research, the Poisson parameter for the strain and fully relaxed II-VI films were assumed to be $\nu \approx 1/3$ ($a_{\parallel} = a_s$) and $\nu = 0$ ($a_{\parallel} = a_{\perp}$), respectively. This in turn leads to equations (3.6) and (3.7) that describe the lattice mismatch for the extreme strain states.

$$\Delta a = \frac{\delta a}{a_s} = \frac{a_{\perp} - a_s}{2a_s} \text{ (strained)} \quad (3.6)$$

$$\Delta a = \frac{\delta a}{a_s} = \frac{a_{\perp} - a_s}{a_s} \text{ (fully relaxed)} \quad (3.7)$$

$\frac{\delta a}{a_s}$ can be deduced from the XRD scan using the Bragg law $n\lambda = 2d \sin \theta$ which could

be rearranged as $\sin \theta = \frac{n\lambda}{2d}$. Here the first derivative of the Bragg equation $\frac{\delta \theta}{\delta d}$ yields

$$(\cos \theta) \delta \theta = - \left(\frac{n\lambda}{2d^2} \right) \delta d. \quad (3.8)$$

By substituting for $n\lambda$ in (3.8) and recognizing that $\delta a = \delta d/4$ for the (004) plane, an expression for δa can be derived as shown in (3.9).

$$\delta a = a_s - a_{\perp} = - \frac{a_s \cot \theta_B}{2} \delta \theta \quad (3.9)$$

where $\delta \theta = \theta_s - \theta_L$.

Using (3.6), (3.7) and (3.9), the equation for the lattice mismatch can be described as shown in (3.10)

$$\frac{\Delta a}{a_s} = \left(- \frac{\delta \theta \cot \theta_B}{2} \right) \left(\frac{1 - \nu}{1 + \nu} \right) \quad (3.9)$$

with $\delta \theta$ expressed in radians.

In order to accurately determine the lattice mismatch or lattice constant, the strain state of the epilayer must be known. The Poisson parameter for most eptaxial films varies from 0.25 to 0.35. In cases where the epilayer is partially relaxed the strain parameter is unknown. In this situation the (115) XRD scan is performed to determine the lattice

constant parallel ($a_{\parallel}$) and perpendicular ($a_{\perp}$) to the (001) plane. Throughout this work, the (115) scan was seldom used because the layers were deliberately grown to be pseudomorphic ($\leq 0.5 \mu\text{m}$) or fully relaxed ($\geq 1.0 \mu\text{m}$).

3.1.3.2 Calculation of Layer Thickness

The XRD technique is frequently used for analyzing multi-quantum well (MQW) structures. During XRD analysis, each of the underlying layers produces a series of satellite peaks from which very important information can be obtained. The quality of the MQW can be deduced from the FWHM of these peaks. Very narrow FWHM is indicative of high quality well/barrier interfaces. Apart from assessing material quality, the satellite peak spacing can be used to accurately determine the periodicity of the MQW structure. Using the Bragg law (3.2) and Fig. 3.10, an equation for calculating the periodicity of the MQW structure can be derived.

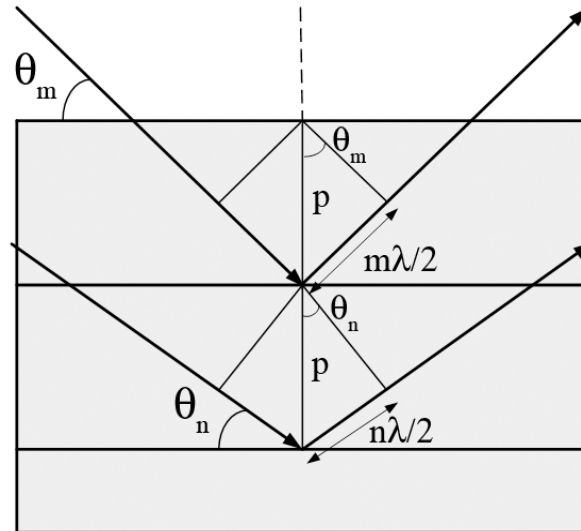


Figure 3.10: Description of path taken by x-ray photons during (004) XRD scan. This diagram explains the periodicity of a MQW sample satellite peaks.

Let $n\lambda = 2p \sin \theta_n$ and $m\lambda = 2p \sin \theta_m$ represent two diffraction orders whose spacing is equal to the periodicity of the MQW structure. This implies that $m - n = 1$ and $\theta_m - \theta_n = \delta\theta$ (the XRD satellite peak separation). The equations for the two diffraction orders can be arranged as follows:

$$\begin{aligned}
m\lambda - n\lambda &= \lambda = 2p \sin \theta_m - 2p \sin \theta_n \\
\Rightarrow \lambda &= 2p \sin(\theta_n + \delta\theta) - 2p \sin \theta_n \\
\Rightarrow \lambda &= 2p [\sin \theta_n \cos \delta\theta + \sin \delta\theta \cos \theta_n] - 2p \sin \theta_n \\
\Rightarrow \lambda &= 2p [\sin \theta_n + \delta\theta \cos \theta_n] - 2p \sin \theta_n \\
\Rightarrow \lambda &= 2p (\sin \theta_n + \delta\theta \cos \theta_n - \sin \theta_n) \\
\Rightarrow \lambda &= 2p \delta\theta \cos \theta_n
\end{aligned}$$

These calculations eventually give rise to equation (3.11) which can be used to calculate the periodicity, p , of a MQW structure.

$$p \approx \frac{\lambda}{2\delta\theta \cos \theta_n} \quad (3.11)$$

where $\delta\theta$ is the satellite peak spacing in radians and θ_n is the Bragg angle of the substrate.

3.2 Photoluminescence

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. During this process the impinging photons from the light source provide enough energy for valence band electrons to transition into the empty states of

the conduction band. In time, these excited electrons spontaneously exit the conduction band through a variety of recombination processes which are illustrated in Fig. 3.11. Therefore, this characterization technique is very useful in assessing the optical properties of semiconductor material.

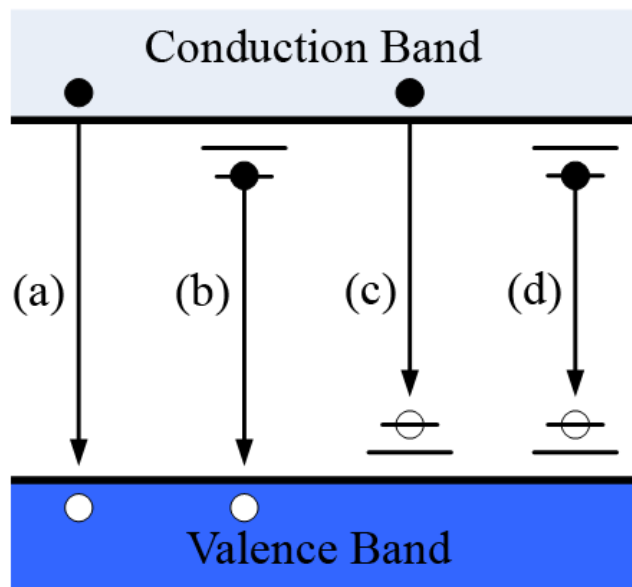


Figure 3.11: Description of some of the common electronic transitions that lead to radiative emission during photoluminescence. (a) Conduction band to valence band (C-V) (b) Donor to valence band (D-V) (c) Conduction band to acceptor level (d) Donor to acceptor level (D-A)

Semiconductors are usually classified as direct or indirect bandgap materials. In direct bandgap materials the conduction and valence band minima are aligned at the point $k = 0$, enabling electronic transitions to occur between the bands with zero change in momentum (see Fig. 3.12). This property is directly responsible for the high rate of radiative recombination and widespread use of direct bandgap materials in the fabrication of optoelectronic devices.

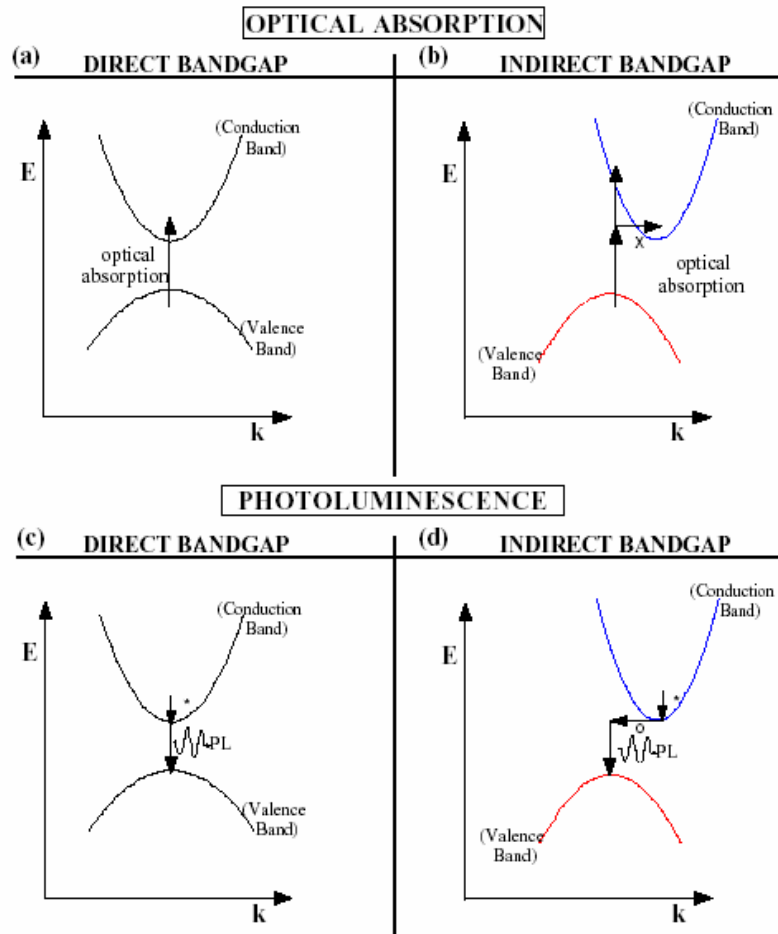


Figure 3.12: Description of optical absorption and photoluminescence in direct and indirect bandgap materials.⁵¹

In the case of indirect bandgap materials the conduction band minimum and valence band maximum are not aligned. During the absorption step it is possible for electronic transition to occur between the top of the valence band and higher energy states in the conduction band with zero change in momentum. These absorbed electrons eventually relax non-radiatively to the bottom of the conduction band as a result of electron/phonon activity. In order for photoluminescence to occur (radiative C-V transitions),

phonon/electron interactions must occur to bring about the necessary momentum change. This requirement dramatically reduces the probability of radiative recombination in indirect bandgap materials making them unsuitable for optoelectronic device production such as lasers.

For high quality direct bandgap material the dominant PL peak is usually the result of conduction band to valence band (C-V) radiative recombination. In cases where there are impurities such as p-type or n-type dopants, secondary emission peaks may be observed due to donor-valence band (D-V) or conduction band – acceptor (C-A) electronic transition. In situations where the semiconductor is compensated (n-type and p-type dopants are present), emission peaks due to donor-acceptor (D-A) transition may be seen. Deep level emission peaks may be observed in cases where material defects are prevalent (e.g threading dislocations). These defects result in the formation of energy states within the bandgap that trap electrons. Radiative recombination involving these trapped electrons usually produces a broad PL peak as shown in Fig. 3.13.

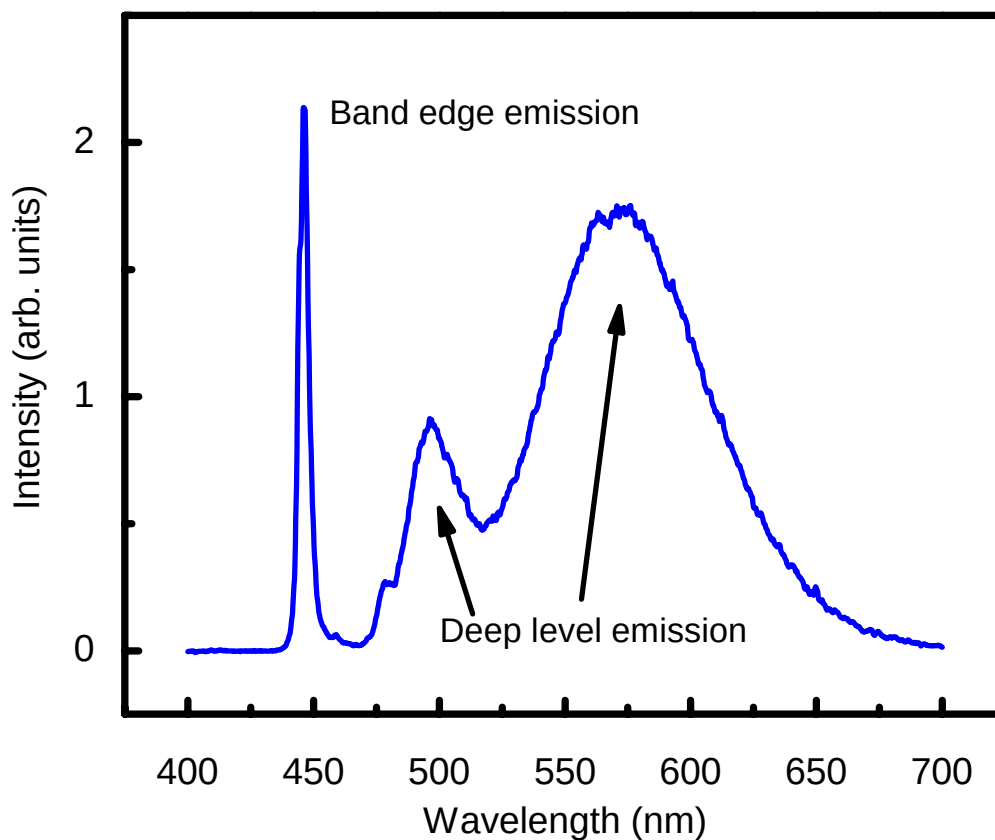


Figure 3.13: Photoluminescence spectrum for a II-VI sample showing band edge and deep level emission.

Deep level emission is an indication of poor quality material. These deep level energy states reduce the amount of conduction band electrons in a semiconductor device. The defects that lead to deep level emission could also limit the lifetime of the device.

Throughout this research, PL analysis was used primarily to determine the bandgap of bulk material and assess the quality of the grown epilayer. MQW samples were also evaluated to get preliminary information about the spacing of the quantized energy levels.

Thickness uniformity of MQW samples and material quality comparisons of bulk material were made by measuring the FWHM of the emission peak. The schematic setup for the PL setup used in this work is shown in Fig. 3.14.

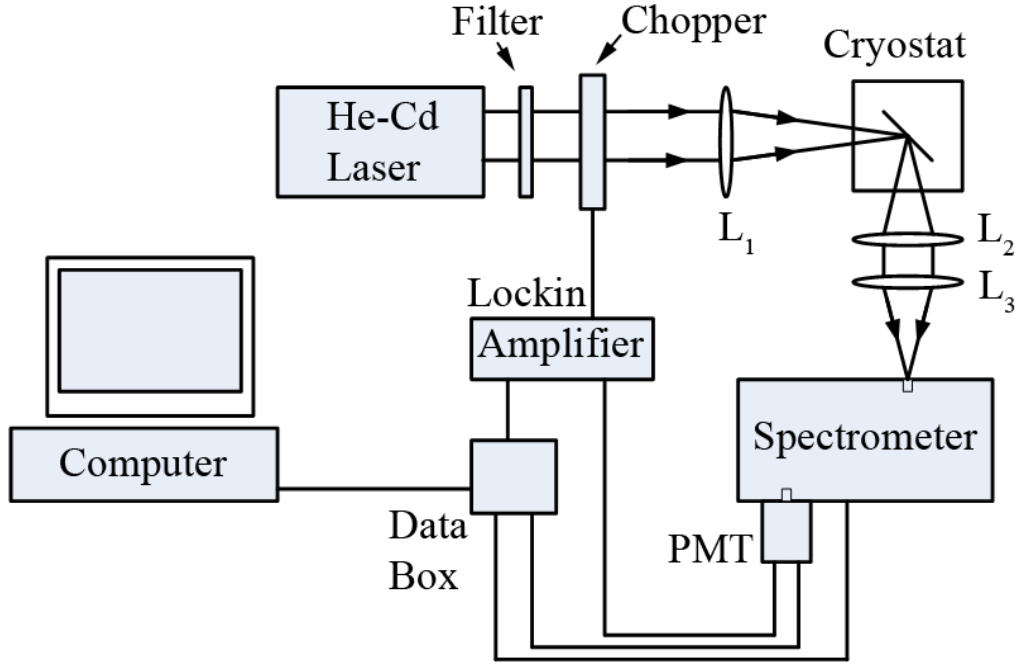


Figure 3.14: Description of photoluminescence setup.

Before starting the PL measurement process, small pieces of the sample of interest were mounted on the cold finger of the Janis Cryostat. The cryostat was then attached to a pump to bring the vacuum down to $\sim 10^{-5}$ torr. Evacuation of the cryostat is an important step since this ensures the removal of gasses that could condense on the cryostat window during low temperature measurements. The cold finger was attached to a temperature controller that could vary the temperature from 5.8 K up to 300 K. The light source for the measurement was a Helium-Cadmium (He-Cd) laser that generates 20mW of light at a central wavelength of $\lambda = 325$ nm. The emitted light from the laser was first passed through a band pass filter that has a 90% transmittance at $\lambda = 325$ nm.

The light from the filter was then passed through a chopper that converts the continuous wave emission to an alternating (AC) signal. This AC signal was focused onto the sample using cylindrical convex lens. The emitted light for the sample was collected and collimated with a convex lens. The collimated light was then focused using a second convex lens. The photomultiplier was connected to the lock-in amplifier which amplified the ac signal generated by the detector. The lock-in amplifier was in turn connected to the Datascan that acts as an interface between the controlling PL software and hardware.

In this research, the cryostat was evacuated if a low temperature PL measurement was required. After evacuation, the cryostat was placed at 45° to the incident laser light as shown in Fig. 3.14. Then, the temperature controller was attached to the cryostat and turned on. Next, the chopper, spectrometer, lock-in amplifier, data box (DataScan) and computer was turned on. The laser was also switched on and allowed to stabilize for at least 20 minutes. During this time, the temperature of the cryostat cold finger was reduced to the desired temperature (typically 77° K). At this time laser light was focused onto the sample. The room light was turned off and the emitted light from the sample was focused and positioned between the slits of the SPEX 1680B spectrometer. The entry slit of the spectrometer and photomultiplier detector were opened to the same setting ($50\text{ }\mu\text{m}$) and the PL software on the computer was used to perform a rough scan. After identifying the wavelength corresponding to the dominant PL emission, the spectrometer was moved to that wavelength. The PL emission position at the spectrometer entry slit or the width of the spectrometer and detector slits were adjusted to ensure that the light received by the detector was of the desired intensity. During the alignment process a neutral density filter was occasionally used to adjust the intensity of the incident laser light. At the end of this

alignment phase the step size and integration time on the PL software was adjusted and a scan was done to produce the final PL spectrum.

3.3 Material Composition Determination

Throughout this research, the material composition for ternary materials was calculated using the lattice constant from XRD analysis and Vegard's law. This law assumes that material lattice constant varies linearly with that of the constituent binaries as described by equation. For ternary materials there is only one unknown, therefore, this linear equation can easily be solved.

$$a_T = a_{(AX)}x + a_{(BX)}(1 - x) \quad (3.12)$$

The lattice constant for the ternary $A_xB_{(1-x)}X$ can be calculated using (3.12). Here, x represents the composition of the binary AX. The lattice constant of the ternary is a_T while $a_{(AX)}$ and $a_{(BX)}$ represent the lattice of the binaries AX and BX. In the case of quaternary materials there are two unknowns in the equation. To obtain the material composition for the quaternary a second equation describing the relationship between quaternary bandgap and the constituent binaries is used. The relationship between the lattice constant and the bandgap of $Zn_xCd_yMg_{(1-x-y)}Se$ can be seen in Fig. 2.1. Here, the ternary and quaternary lattice constants do not vary linearly with bandgap. The relationship between the bandgap and material composition is as expressed in equation (3.13).

$$E_g(x, y) = ax^2 + by^2 + cxy + dx + ey + f \quad (3.13)$$

The lattice constant and bandgap for the constituent II-VI binaries at 10 K are displayed in Table 1.

Binary	Lattice Constant (Å)	Bandgap (eV)
ZnSe	5.6676	2.8215
CdSe	6.052	1.78
MgSe	5.89	3.65

Table 3.1: Lattice constant and bandgaps for II-VI binaries

From Fig. 2.1, the bandgap of $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$ ($E_g(1,0)$) and $\text{Cd}_y\text{Mg}_{(1-y)}\text{Se}$ ($E_g(0,1)$), vary linearly with the composition of their binaries. With this in mind the coefficients for (3.13) were found as follows:

Set $x = 0$ to get an equation for $\text{Cd}_y\text{Mg}_{(1-y)}\text{Se}$

$$E_g(0, y) = by^2 + ey + f \quad (3.14)$$

The fact that the equation for this ternary must be linear implies that $b = 0$. Furthermore, the coefficients e and f can be found by using the bandgaps of CdSe ($y = 1$) and MgSe ($y = 0$). Here the coefficients e and f were determined to be -1.87 and 3.65, respectively.

Similarly, when $y = 0$ in (3.13) an equation was obtained for $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$.

$$E_g(x, 0) = ax^2 + dx + 3.65 \quad (3.15)$$

Given that (3.15) should be linear and the bandgap for ZnSe ($x = 1$) is known, the coefficients a and d were found to be 0 and -0.83, respectively. This leads to an intermediate (3.16) where the coefficient c is the only unknown.

$$E_g(x, y) = cxy - 0.83x - 1.87y + 3.65 \quad (3.16)$$

When $x + y = 1$, the magnesium composition is zero. By substituting $x = 1 - y$ into equation (3.16), the relationship between the ternary $\text{Zn}_{(1-y)}\text{Cd}_y\text{Se}$ bandgap and its composition can be found (3.17). Moreover, the final coefficient was determined to be $c = -0.35$.

$$E_g(y) = 0.35y^2 - 1.39y + 2.82 \quad (3.17)$$

The general equation for the quaternary bandgap is

$$E_g(x, y) = -0.35xy - 0.83x - 1.87y + 3.65 \quad (3.18)$$

Using Vegard's law an equation for the quaternary $\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ can be expressed as follows:

$a(x, y) = ax + by + c(1 - x - y)$ where a , b , and c represent the lattice constants of ZnSe , CdSe and MgSe so that $a(x, y) = 5.667x + 6.076y + 5.89(1 - x - y)$. Upon further simplification the Vegard's equation for the quaternary is

$$a(x, y) = -0.223x + 0.186y + 5.89 \quad (3.19)$$

After determining the lattice constant and bandgap by XRD and PL analysis of the quaternary sample, its composition can be easily found by simultaneously solving equations (3.18) and (3.19).

3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is one of the material characterization techniques that were used in this research to analyze thin film semiconductor structures. The electron column of a typical SEM system is shown in Fig. 3.15. At the top of the column is an electron gun that could be of two types. The first type is the thermionic emission gun where electrons are produced from a heated tungsten hairpin or a lanthanum hexaboride (LaB_6) filament that forms the cathode. The second type is the field emission electron gun where electrons are stripped from the pointed tip (tip radius $\leq 100 \text{ nm}$) of the cathode by a strong electric field. These SEM sources generate and accelerate electrons up to an energy of $0.1 - 30 \text{ KeV}$. Beneath the electron gun are two magnetic lenses (referred to as condensers) that are used to adjust the spot size of the electron beam. The resolution of this equipment is directly related to the spot size of the electron beam. A SEM equipped with thermionic filaments produces a minimum spot size of about 10 nm while those with field emission guns can produce a minimum spot size of $\sim 1 \text{ nm}$.⁵² The final magnetic or objective lens is responsible for the fine focusing of the electron beam onto the sample. Embedded in the objective lens are scan coils that are used for scanning the electron beam on the surface of the sample. Also present are coils that are responsible for astigmatism control. At the base of the electron column are vacuum pumps that enable pressures of $10^{-5} - 10^{-8} \text{ torr}$ to be obtained. High vacuum is necessary to protect the electron gun filament (or pointed tip) and reduce the incidence of electron scattering.

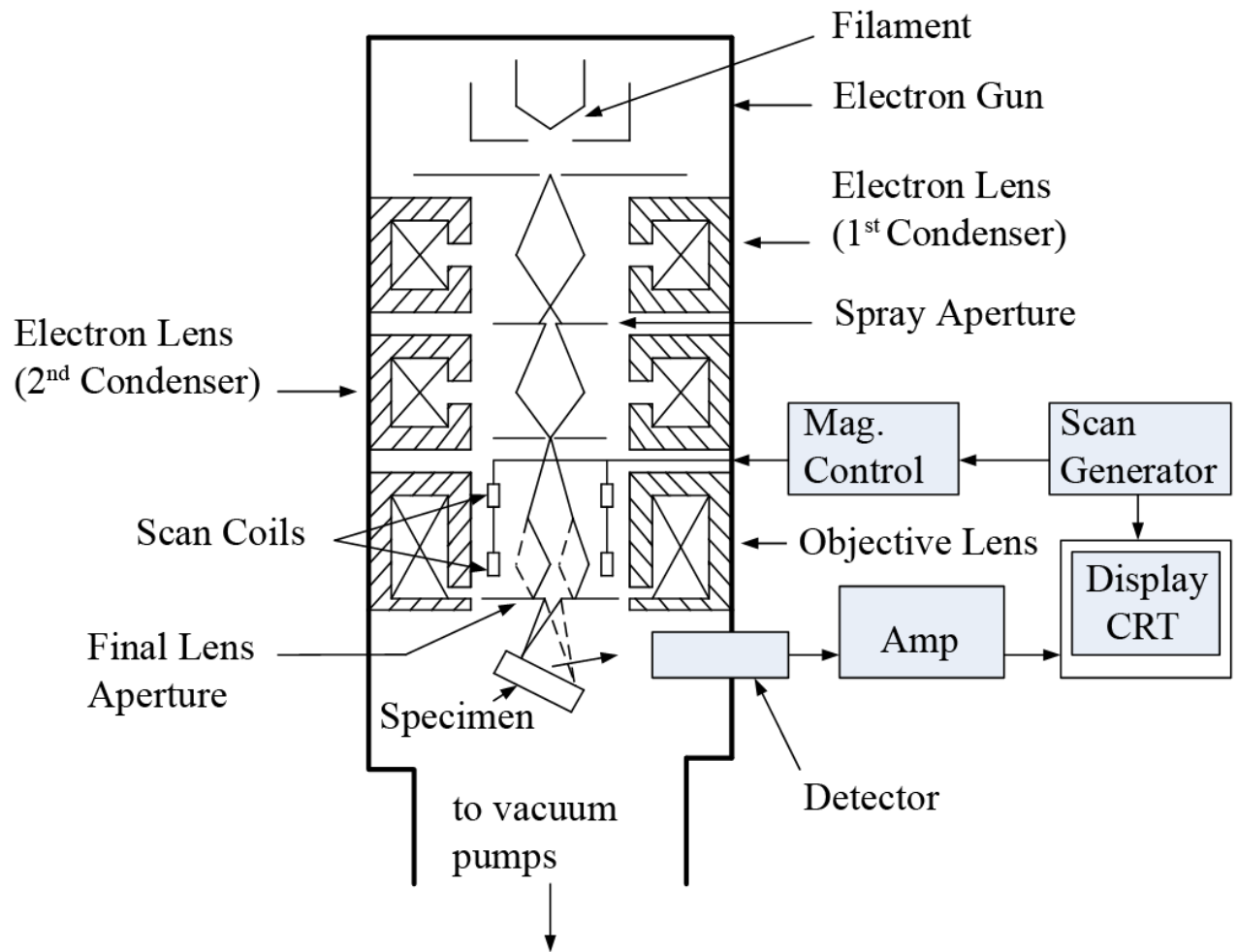


Figure 3.15: Schematic diagram of a scanning electron microscope.⁵³

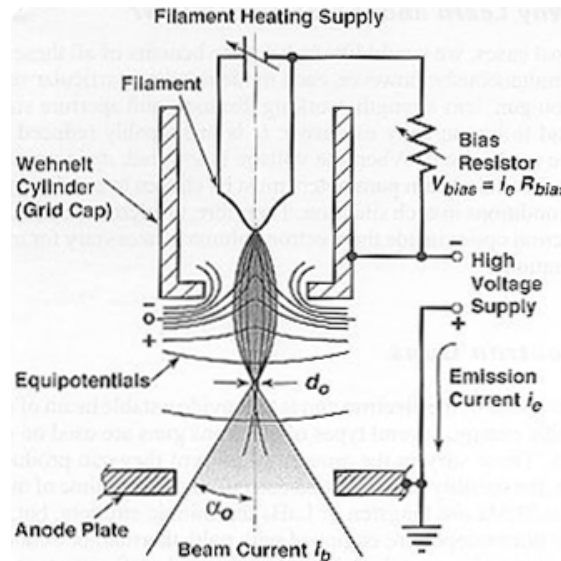


Figure 3.16: Description of SEM electron gun with hairpin tungsten filament.⁵⁴

When the electron beam is brought to a focus on the sample, the bombardment of the sample with high energy electrons result in the production of x-rays, backscattered (BSE) and secondary electrons (SDE) forming an interaction volume at the point of impact. These emitted electrons and radiation are collected using a detector system as described in Fig. 3.17.

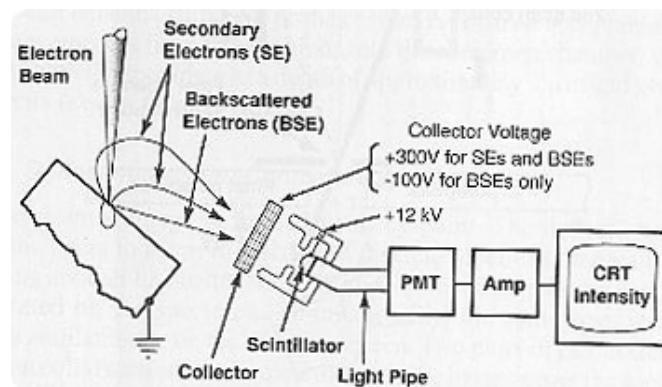


Figure 3.17: Schematic representation of electron detection in a SEM system.⁵⁵

The x-ray signal can be used to identify the elements in the sample. In SEMs that are equipped with an electron probe micro-analyzer (EPMA), the sample surface could be analyzed in a raster fashion to map the location of various elements. With this capability, the material composition can be ascertained to accuracy of 1- 2 % for flat polished samples. The BSE are electrons that emerge from the sample surface due to a series of elastic collisions with the sample (or specimen) atoms. As BSEs exit crystalline samples, interference patterns are formed that reveal structural details about the material. This has led to the use of BSEs for structural analysis of crystalline samples. SDEs are produced when the impinging high energy electrons completely remove electrons from the orbitals of sample atoms. During the SEM scan, the focused electron spot is swept in a raster fashion, forming an interaction volume containing SDEs and BSEs at every point. These SDEs and BSEs, are collected by the detector as shown in Fig. 3.17, revealing highly magnified topographical details of the sample. Hence, SDEs and BSEs are primarily used for obtaining highly magnified images of samples. Throughout this research, SEM was used for viewing the cross-section of thin film semiconductors. This was done for the purpose of determining the thickness of bulk material. This thickness information was used to calculate the growth rate of the epilayer. SEM cross-section images of samples were also taken to determine the quality of the well/barrier interfaces in MQW structures.

3.5 Hall Effect

The Hall effect is widely used in the semiconductor industry to ascertain the carrier characteristics of semiconductor materials. Hall effect measurements are based on the fact that as charged particles traverse a magnetic field, a force is generated that pushes them to a particular side of the conductor in accordance with the Lorentz equation (3.20).

$$F = q\bar{v} \times \bar{B} \quad (3.20)$$

Here q is the magnitude of an electron charge, $\bar{v}$ is the drift velocity of electrons or holes and $\bar{B}$ is the applied magnetic field. This measurement technique is used on semiconductor materials as described in Fig. 3.18 to determine the majority carrier type, concentration, mobility and resistivity.

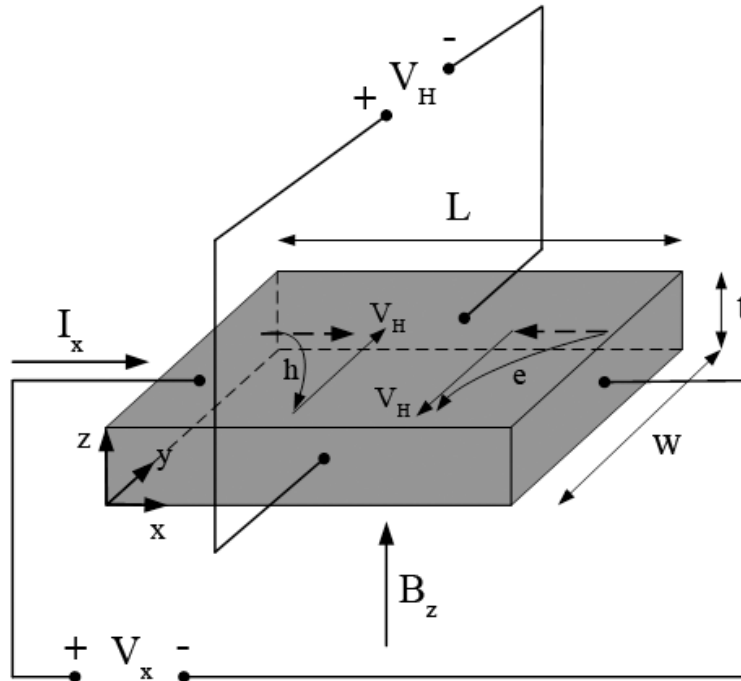


Figure 3.18: Description of Hall effect in semiconductor materials.⁵⁶

For an applied current I_x as shown in Fig. 3.18, the majority carrier would be deflected in the $-y$ direction and thus accumulate on the $y = 0$ side of the material. This build up of majority carriers on one side of the semiconductor material results in the formation of a measurable potential difference, V_H , perpendicular to the flow of the current, I_x . Here the sign of Hall voltage V_H depends on the majority carrier type. For p-type material the Hall voltage is positive while for n-type material the opposite is true. In steady state, the force that is responsible for charge deflection is completely balanced by the created electric field (Hall field).

$$F = q(E_H + \vec{v}_x \times \vec{B}_z) = 0 \quad (3.21)$$

Given that the Hall field between two parallel sides of the semiconductor shown in

Fig. 3.18 is $E_H = \frac{V_H}{w}$ (where w is the distance between the parallel sides), equation

(3.21) can be arranged to produce an equation for the V_H .

$$V_H = v_x w B_z \quad (3.22)$$

The drift velocity of holes and electrons in a semiconductor is generally expressed as

$$v_x = \frac{I_x}{(wt)(qp)} \quad \text{for p - type} \quad (3.23)$$

$$v_x = -\frac{I_x}{(wt)(qn)} \quad \text{for n - type} \quad (3.24)$$

where n and p are the electron and hole concentrations. Using a combination of (3.22), (3.23) and (3.24) the carrier concentration of the semiconductors can be expressed as follows:

$$n = -\frac{I_x B_z}{q V_H t} = -\frac{1}{q |R_H|} \quad (3.25)$$

$$p = \frac{I_x B_z}{q V_H t} = \frac{1}{q |R_H|} \quad (3.26)$$

$|R_H| = \frac{|V_H| t}{I_x B_z}$ represents the magnitude of the Hall coefficient where V_H is always negative for n-type semiconductor material. The opposite is true for p-type semiconductor material.

The carrier mobility is directly related to electron and hole scattering as these carriers attempt to flow across the conductive material. During the current flow, the electrons and holes are scattered by ionized impurity atoms (e.g donor and acceptor ions) and other defect sites in the crystal lattice. Mobility due to ionized impurities and lattice defects are represented by μ_i and μ_L , respectively. The relationship between the scattering events and the overall mobility of the material is described by equation (3.27). This equation suggests that a low overall mobility, μ , is an indicator of high doping levels or poor material quality.

$$\frac{1}{\mu} = \frac{1}{\mu_i} + \frac{1}{\mu_L} \quad (3.27)$$

The mobility of semiconductor material is directly related to the conductivity of the material.

$$\sigma = q(\mu_n n + \mu_p p) \quad (3.28)$$

For n-type material where $n \gg p$, $\sigma \approx q\mu_n n$ while for p-type material where

$p \gg n$, $\sigma \approx q\mu_p p$. Given that the drift current in semiconductor material is

$J_x = \left(\frac{I_x}{wt} \right) = \sigma E_x$ and $E_x = \frac{V_x}{L}$, the mobility of the carriers can be written as follows:

$$\mu_n = \frac{I_x L}{qnV_x wt} \quad (3.29)$$

$$\mu_p = \frac{I_x L}{qpV_x wt} \quad (3.30)$$

By making the relevant substitution in (3.29) and (3.30) for n and p , the mobility for the electrons and holes could be expressed in terms of the semiconductor resistivity ρ and the Hall coefficient R_H .

$$\mu_n \text{ or } \mu_p = \frac{|R_H|}{\rho} \quad (3.31)$$

Throughout this research, the Van der Pauw Hall measurement technique was employed. Here the semiconductor was cleaved into a 5 mm x 5 mm square and gold wires were attached to the four corners of the semiconductor using indium. These four electrical contacts were used for current injection and voltage measurements as described by the Van der Pauw technique.^{57, 58} These experiments were usually carried out by applying a 100 μ A of current using a Kiethely 220 programmable current source and the current passing through the semiconductor was measured with a Keithely 6485 picoameter. Hall measurements were carried out using a fixed magnetic field of 2.5 KG. All voltage measurements across the semiconductor were done using a Keithely 182 volt meter. Figure 3.19 provides a description of the Hall effect measurement system used in this dissertation.

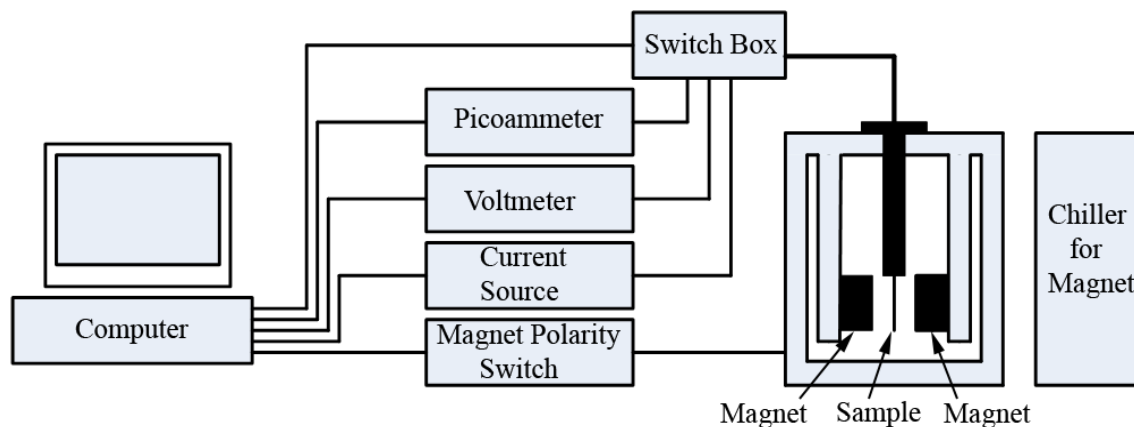


Figure 3.19: Hall system used for determining carrier characteristics of doped semiconductor samples.

3.6 FTIR Spectroscopy

FTIR spectroscopy is based on the operating principles of the Michelson interferometer. This instrument was developed by Albert Abraham Michelson in 1880 for the sole purpose of answering the question concerning the existence of “luminiferous aether,” which scientists at that time proposed must have existed for the propagation of electromagnetic radiation. In 1907, Michelson received the Nobel Prize in physics for accurately measuring wavelengths of light with this instrument.⁵⁹ The Michelson interferometer is composed of a 50/50 beam splitter that has two mirrors of equal reflectivity (ideally 100%) and a detector arranged as shown in Fig. 3.20.

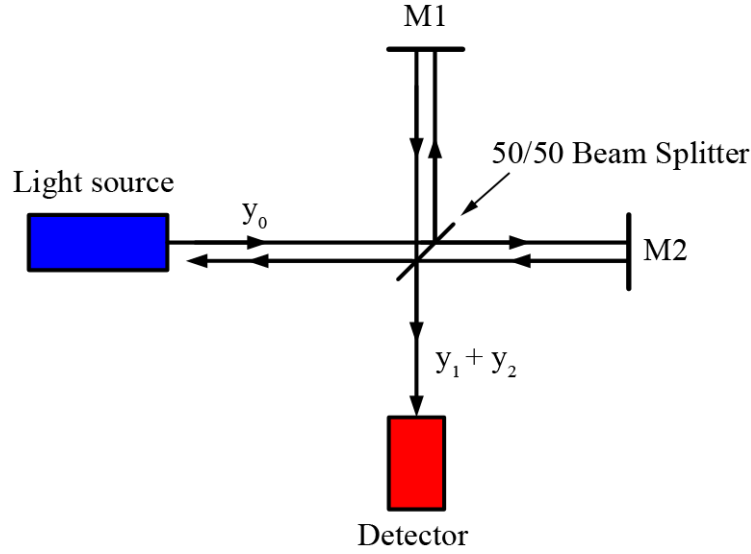


Figure 3.20: Description of the Michelson interferometer. In the FTIR system, one mirror is fixed while the displacement of the second varies.

The beam splitter divides the incident light into a reflected and a transmitted beam with each beam having half the intensity of the incident light. If the distance between the beam splitter and mirror M1 and M2 are equal, the light reaching the detector will have maximum intensity. For this mirror arrangement, the phase difference between the two beams is zero resulting in constructive interference of the two light beams. In situations where the displacement of M1 and M2 are different, it is possible that destructive interference may occur. To further understand the behavior of the Michelson interferometer let $y_1 = A_1 \exp(-j[\omega t + kz])$ and $y_2 = A_2 \exp(-j[\omega t + kz - kd])$ represent the fraction of the reflected light from mirror M1 and M2 that make it back to the detector. For mirrors with identical reflectivity (let us assume 100% reflectivity), the intensity of the reflected light will be the same, resulting in $A_1 = A_2 = \frac{I_o^{1/2}}{2\sqrt{2}}$. The equation

for the light that enters the detector can be computed as follows:

$$I = |y_1 + y_2|^2 = y_1^2 + y_2^2 + y_1 y_2^* + y_1^* y_2$$

$$I = \frac{I_0}{4}(1 + \cos(kd)) \quad (3.32)$$

where $k = \frac{2\pi}{\lambda}$. When the path difference $d = n\lambda$ ($n = 0, 1, 2, \dots$), the intensity is at its maximum ($I_0/2$). On the other hand, when $d = (n + 1/2)\lambda$ ($n = 0, 2, 4, \dots$), the intensity is zero. A plot of the intensity of the detected light vs. path difference for monochromatic light would produce a cosine wave. Furthermore, when light of wavelength λ_1 and λ_2 are directed into the interferometer and an intensity vs. path difference plot is made, the end result is a superposition of sinusoidal waves for the two mirrors. The Michelson interferometer used in FTIR instruments are modified such that the displacement of mirror M1 is fixed while that of M2 is variable. This variability of M2 enables the generation of sinusoidal waves for all the frequency components of the incident light. When the displacements of the two mirrors are equal, the wavelengths that make up the incident light have zero phase difference, and therefore interfere constructively. This produces the centerburst in the FTIR interferogram show in Fig. 3.21. When the displacement of M2 changes, the individual wavelength components that make up the light begin to interfere destructively, giving rise to the wing segments of the interferogram.

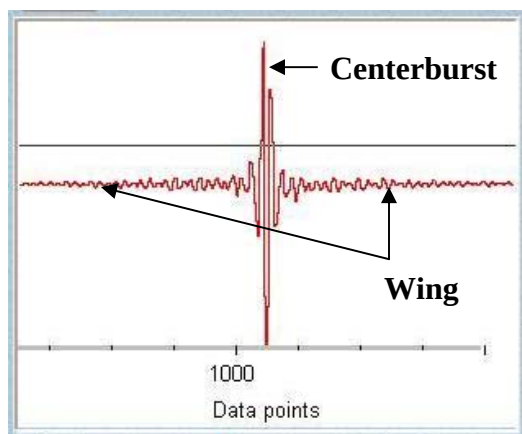


Figure 3.21: FTIR interferogram showing the centerburst and wing sections.

The first commercial FTIR system was produced in the 1960s. Commercialization of this instrument was due to the development of the fast Fourier transform (FFT) algorithm, and advances in computer technology. Modern computers with their large storage capacity and high processing capabilities enabled quick processing of the detector's electrical data using the FFT algorithm. With this algorithm the interferometer data is transformed into a spectrum that shows a relationship between light intensity and the inverse wavelength (wavenumber).

The FTIR spectroscopy process usually begins with the cooling of the detector using liquid nitrogen (if a mercury cadmium telluride (MCT) detector is used). Following this step, the FTIR control software is used to select the number of scans, mirror speed and the resolution desired for collecting the spectrum. The number of scans is indicative of the number of cycles made by the variable mirror to produce the final spectrum. A large number of scans is recommended since the effects of random noise is averaged out as the number of scans are increased (improved SNR). The mirror speed determines how long it takes for the variable mirror to complete a cycle, hence it influences the

integration time. The resolution determines the number of data points that are collected during a scan. A high resolution is necessary for resolving very narrow spectral features.

A background spectrum is first collected with the sample absent from the light path. This single beam spectrum may show absorption at 3500 and 1630 cm^{-1} due to the presence of moisture. Absorption features may be seen at 2350 and 667 cm^{-1} due to the presence of atmospheric carbondioxide. The sample is then placed in the beam path and a single beam spectrum is collected in the same manner as the background. In order to observe the absorbance of the sample the background and sample data must be treated as described by (3.33).

$$A = -\ln\left(\frac{\text{Sample Data}}{\text{Background Data}}\right) \quad (3.33)$$

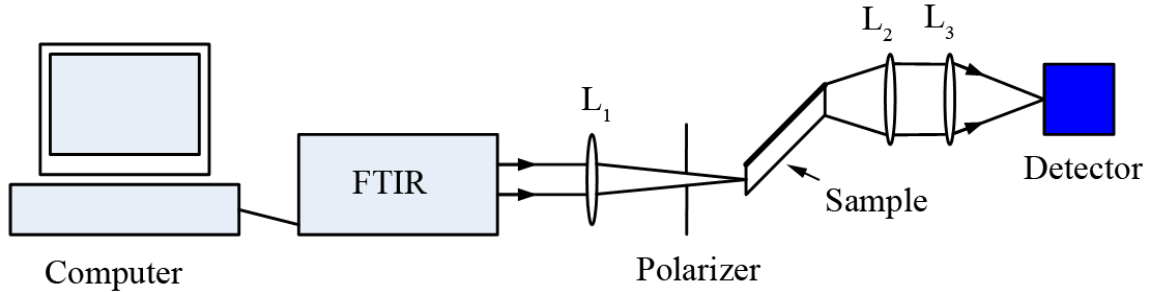


Figure 3.22: Schematic description of FTIR system with external optics and detector.

FTIR spectroscopy was used in this research to measure intersubband (ISB) absorption in MQW samples. The sample was first process in the waveguide with 45° facets as shown in Fig. 3.22. External optics and MCT detector were used in this experiment. A zinc selenide (ZnSe) lens was used to focus the incident IR light onto a polished facet of the thin waveguide. The transmitted light from the second polished facet was collimated and then focused into the MCT detector using a second set of ZnSe

lenses. Due to the fact the ISB absorption only occur when the electric field light is perpendicular to the growth direction, a ZnSe based polarizer was used to control the orientation of the incident light. First backgrounds were collected for transverse magnetic (TM) and transverse electric (TE) polarized light by inserting the polarizer between the IR light source and the detector. This was then followed by the collection of single beam spectra for the sample. In this instance, the polarizer was place between the IR source and the sample. A single beam spectrum was collected with the polarizer in the TM and TE positions, respectively. The absorbance for MQW samples were calculated as shown in equation (3.34)

$$A = -\ln\left(\frac{A_{TM}}{B_{TM}}\right) + \ln\left(\frac{A_{TE}}{B_{TE}}\right) \quad (3.34)$$

where A and B represent the sample and background single beam data.

3.7 Contactless Electroreflectance (CER)

The determination of a semiconductor material's bandgap is usually done using photoluminescence measurements; on the other hand, ISB transitions within MQW structures are most commonly determined using FTIR absorption spectroscopy. The CER technique is attractive because it is non-destructive and it is capable of providing all of this information with minimal sample preparation. Moreover, this technique is ideally suited for determining the CBO of novel semiconductor materials.

The typical setup of a CER system is shown in Fig. 3.23. Here, the light from a 150 W xenon-arc or tungsten halogen lamp is directed into a monochromator. The exit light for the monochromator at wavelength λ is passed through a variable neutral density

filter (VNDF) so that the intensity, $I_0(\lambda)$, can be adjusted as required. The light from the VNDF is focused onto the sample in a condenser-like sample holder as described in Fig. 3.23 b. The sample is attached to the back electrode using vacuum grease. The front electrode of this sample holder is a wire grid that is held ~ 0.1 mm from the sample surface by insulating spacers. The back electrode is attached to ground while the front electrode is attached to an oscillating high voltage. During the measurement a voltage of 1 KV peak to peak is applied between the electrodes. This voltage is usually modulated at a frequency of $\Omega_m = 1$ Hz. The reflected light from the sample is collected and focused onto the silicon based photodetector.

The reflected light which is focused onto the detector is composed of both dc and ac components. The dc portion of the light is described as $(I_0(\lambda)R(\lambda))$ where $R(\lambda)$ is the dc reflectance. Similarly, the ac portion of the light is described as $I_0(\lambda)\Delta R(\lambda)$ where $\Delta R(\lambda)$ is the change in the reflectance due to oscillating high voltage (Ω_m : frequency of voltage oscillation) between the electrodes of the sample holder. The ac signal from the detector is fed back into the lock-in amplifier. In order to eliminate the uninteresting dc light, normalization is performed using both the signal from the VNDF/servo and the detector. This normalization is achieved by varying the VNDF so as to maintain a balance between the signal for the servo and the detector. As a result, only the modulated signal, $\Delta R(\lambda)$, that is superimposed on the dc light is displayed as the CER output. The CER spectrum produces sharp derivative-like features corresponding to electronic transition between valence and conduction band energy levels.

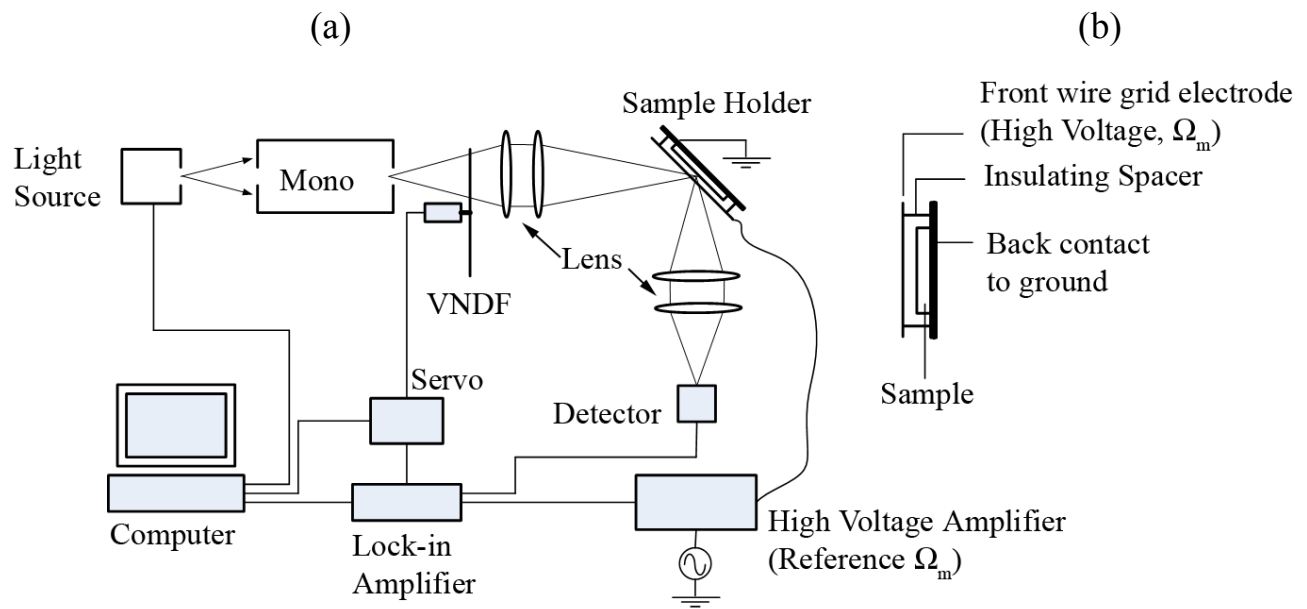


Figure 3.23: (a) Schematic illustration of contactless electro-reflectance system (b)

Description of sample holder showing contactless mechanism.

Chapter 4

Previous Work with $\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ Materials

In order to design a QC laser and accurately predict its optical properties, the material parameters such as the electron effective mass and conduction band offset (CBO) must be known. Over the years, due to the widespread use of III-V materials in the optoelectronics industry, this material system has been thoroughly researched to establish their material parameters. The same cannot be said for the II-VI material system since they are seldom used for optoelectronics device production. As a result, the effective masses and CBO are not well established. In 2003 our research group at The City College of New York decided to undertake the task of determining the CBO of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ multi-quantum well (MQW) samples using the contactless electro-reflectance (CER) technique. To this end, a series of MQW sample were grown to evaluate the accuracy of the CBO estimate and FTIR absorption spectroscopy was used to corroborate the accuracy of the design.^{28,60-62} Also, the FTIR spectroscopy study had the added importance of confirming the presence of intersubband absorption in this wide bandgap material system. This was the first indicator that this material system was a viable candidate for QC laser production. The material quality of these MQW samples was assessed using high resolution x-ray diffraction studies (HRXRD) and photoluminescence (PL). With these characterization techniques, we were able to demonstrate that device grade II-VI material can be grown lattice matched to InP.^{62,63}

4.1 Determination of II-VI Material CBO and Effective Masses

The initial work on determine the CBO of this II-VI material system was done by Muñoz et al in 2003.²⁸ This research work was done using a single quantum well (QW) structure. First a 0.1 μm InGaAs buffer layer was grown (001) InP in the III-V chamber. The sample was then transferred under vacuum to the II-VI chamber where an interfacial layer of $\sim 70 \text{ \AA}$ $\text{Zn}_{0.53}\text{Cd}_{0.47}\text{Se}$ was deposited followed by the growth of the II-VI QW structure. The full details of the growth procedure can be found in Ref. 33. The II-VI structure under study consisted of a $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}$ QW, top and bottom barrier layers ($\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$) with nominal thicknesses of 50 $\text{\AA}$, 0.5 and 0.1 μm , respectively. Before ending the growth the structure was capped with 70 $\text{\AA}$ $\text{Zn}_{0.53}\text{Cd}_{0.47}\text{Se}$ cap layer to prevent oxidation of the magnesium in the barrier layers. Bulk ternary and quaternary layers were grown to determine the amount of strain or lattice mismatch. Using x-ray diffraction, the lattice mismatch of the ternary and quaternary layers were determined to be $\Delta a/a = 0.1\%$ and $\Delta a/a = 0.05\%$, respectively. The bulk samples were assessed with photoluminescence (PL) to determine the bandgaps. In this study, the bandgaps of the quaternary was 2.88 eV at 77 K and 2.80 eV at room temperature. The bandgap of the ternary was obtained by performing CER measurements on bulk material grown using the same growth conditions as the single QW II-VI structure. The ternary bandgap was found to be 2.08 eV in good agreement with in Ref. 64 which reported $E_0 = 2.078 \pm 0.002$ and a spin-orbit splitting of $\Delta = 0.442 \pm 0.2 \text{ eV}$.

Room temperature CER analysis was performed on the single QW structure as described in Fig. 4.1.

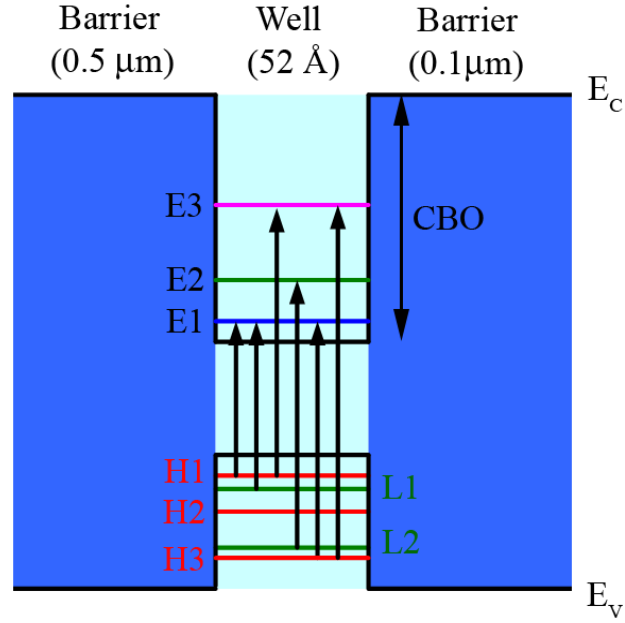


Figure 4.1: Description of a single quantum well that was used to determine the conduction band offset of the II-VI material system. The vertical arrows in the well represent some of the electronic transitions due to CER electric field modulation.

The CER results can be seen in Fig. 4.2 with the solid line representing the CER spectrum. The transition energies were obtained by performing a fit based on the first derivative of a Gaussian line shape.^{65,66} This fit is shown as a dashed line in the Figure.

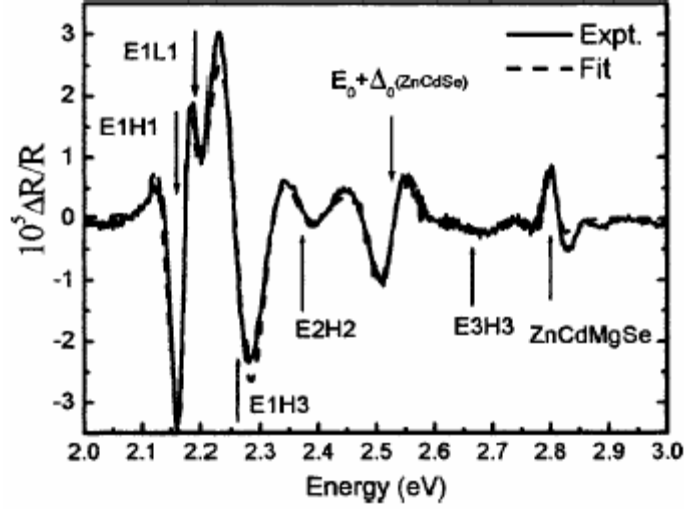


Figure 4.2: Room temperature CER spectrum for a single quantum well structure.

The solid line represents the experimental CER spectrum while the dashed line is the result of a fit that was performed to determine the transition energies in the entire II-VI structure.²⁸

Parameter	ZnSe	CdSe	MgSe	Zn _{0.27} Cd _{0.23} Mg _{0.50} Se	Zn _{0.53} Cd _{0.47} Se
eV				2.80 ^a	2.08 ^a
m_e	0.15 ^b (0.13 – 0.17)	0.11 ^c	0.23 ^d	0.18	0.13
m_{hh}	0.66 ^b (0.57 – 0.75)	0.44 ^c	0.78 ^d	0.67	0.56
m_{lh}	0.145	0.09	0.33 ^d	0.22	0.11
Δ_0 (eV)	0.43 ^e	0.42 ^e	0.40 ^d	0.414 ^f	0.442 ^a
QW (Å)				50 (experiment.), 51.9 (calculated)	
$Q_c = \Delta E_c / \Delta E_0$				0.82 ± 0.002 (calculated)	

^aExperimental Value, ^bAverage of values shown in parentheses, these values were obtained from Ref. 67, ^cRef. 67, ^dRef. 68, ^eRef. 69, ^fInterpolated values using the binary values

Table 4.1: Material parameters used to calculate energy level distribution in II-V quantum wells.²⁸

A simulation based on the Schrödinger's equation was performed to determine the energy level distribution in the quantum well. The material parameters used in this simulation can be found in Table 4.1. The predicted transition energies due to CER analysis and simulation are compared in Table 4.2. In order to determine $Q_c = \Delta E_c / \Delta E_0$ which is the same as $CBO / (E_{0,barrier} - E_{0,well})$, simulations were carried out using varying values of Q_c . These results can be seen in Fig. 4.3. The optimum Q_c value, i.e. the one that best agrees with the experimental values, for the II-VI material system is ~ 0.82 . This implies that the CBO can be calculated as follows:

$$CBO = (E_{0,barrier} - E_{0,well}) \times 0.82.$$

Transition	RT CER (eV)	Theory (eV)
<i>E1H1</i>	2.159 ± 0.005	2.158
<i>E1L1</i>	2.192 ± 0.005	$2.180^a, 2.185^b$
<i>E1H3</i>	2.259 ± 0.005	2.261
<i>E2H2</i>	2.369 ± 0.005	2.371
<i>E3H3</i>	2.660 ± 0.005	2.664
$E_0 + \Delta_0$	2.525 ± 0.005	2.522^c
$E_0(ternary)$	2.800 ± 0.005	

^aCalculation with considering strain, ^bCalculation considering strain,

^cCalculated using Δ_0 from Ref. 64 and our value of E_0 .

Table 4.2: Comparison of transitions energies in a 50 Å thick single quantum well. The experimental data was obtained from curve fitting the CER spectrum while the theoretical information is the result of a simulation using the data in Table 4.1.²⁸

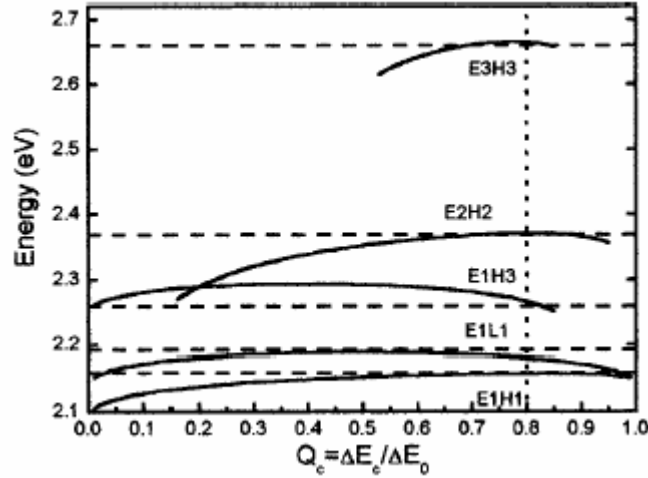


Figure 4.3: The solid dark line in this Figure show the calculated energy distribution in a single QW II-VI structure with varying Q_c values. The dashed horizontal lines show the energies observed in the CER spectrum. The vertical dashed line was drawn at the point where most of the solid curves intersect the CER data. This vertical line represents the optimum Q_c value for the II-VI material system.²⁸

4.2. Intersubband Absorption in $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$

Lu, et al was the first to predict intersubband (ISB) absorption in a multi-quantum well (MQW) structure II-VI using the CER technique and further confirm this using FTIR absorption spectroscopy.⁶⁰ To accomplish this, a

$\text{Zn}_{0.50}\text{Cd}_{0.50}\text{Se}/\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$ QWs structure was grown using MBE. The nominal thickness of the well and barrier layers were 50 and 140 Å respectively and the structure was capped with 90 Å of CdSe. In order to calculate the theoretical energy level distribution in this sample, the effective masses and spin orbit-splitting parameter was calculated using the data in for the II-VI binaries in Table 4.1. The bandgap of the quaternary and ternary material was obtained from the CER spectrum at room

temperature (3.0 eV for quaternary and 2.1 eV for the ternary). The CER spectrum for this sample is shown in Fig. 4.4 while the energy level distribution predicted by CER and simulation is shown in Table 4.3.

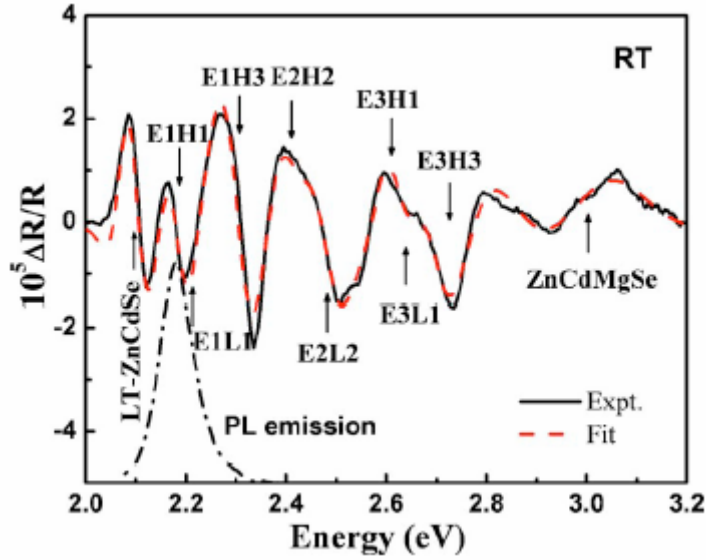


Figure 4.4: Room temperature CER spectrum for a II-VI sample consisting of 10 isolated quantum wells.⁶⁰

Transition	RT CER (eV)	Theory (eV)
$E1H1$	2.183	2.181
$E1L1$	2.205	2.205
$E1H3$	2.306	2.300
$E2H2$	2.412	2.405
$E2L2$	2.483	2.496
$E3H1$	2.608	2.606
$E3L1$	2.633	2.630
$E3H3$	2.726	2.725
$E_0(\text{quaternary})$	PL: 3.113 (77 K) CER: 3.000 (RT)	
$E_0(\text{ternary})$	PL: 2.105 (RT) CER: 2.098	

Table 4.3: Energy level distribution for a II-VI structure consisting of 10 isolated QWs. The table show a comparison between results obtained from CER and simulation.⁶⁰

After performing the CER analysis on the II-VI QW structure, simulations were carried out to determine energy values that would produce a result similar to those predicted by the CER technique. It is only after obtaining a convergence between the results from the theoretical calculations and CER that the energy level distribution in the QWs can be estimated. Using the CER data in Table 4.3, $E_1 \rightarrow E_2$ ISB absorption is estimated to be 178 meV. In an effort to directly measure the $E_1 \rightarrow E_2$ ISB absorption energy, the sample was processed into a waveguide and subjected to FTIR spectroscopy. The results of this measurement can be seen Fig. 4.5.

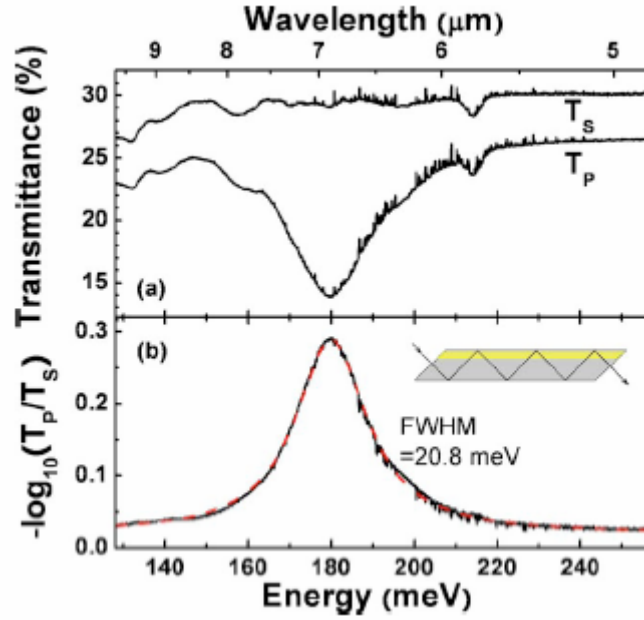


Figure 4.5: FTIR absorption spectroscopy results for a MQW sample with 10 uncoupled QWs 52 Å thick. Based on CER analysis for this sample, $E_1 - E_2$ ISB absorption at 178 meV was expected and absorption at 180 meV was observed. The waveguide geometry of the sample can be seen as an inset.⁶⁰

4.3. High Resolution X-ray Diffraction Characterization of Multi-quantum Well Structures

Apart from investigating ISB absorption in the II-VI materials system Lu et al assessed the material quality of the MQW structure using high resolution x-ray diffraction. The numerous satellite peaks and thickness fringes shown in Fig. 4.6 suggest that device grade MQW structures can be grown using this II-VI material system.

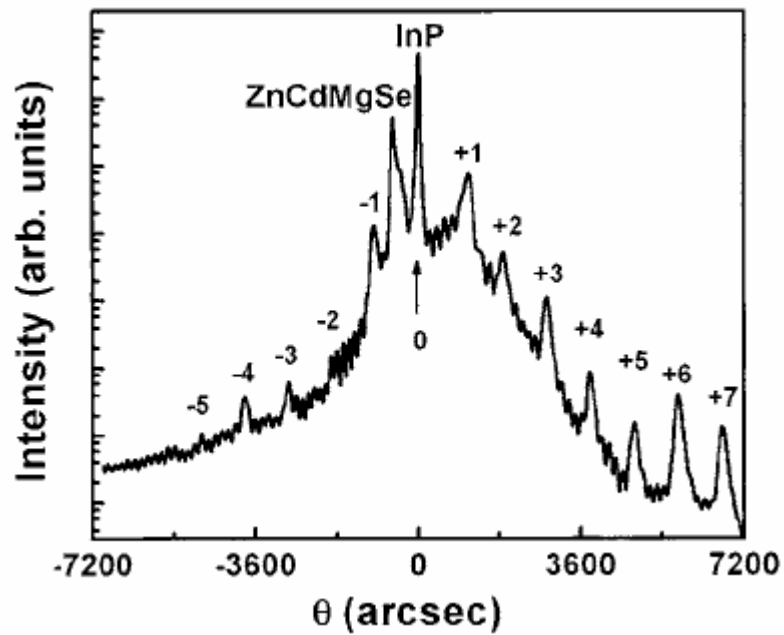


Figure 4.6: High resolution x-ray diffraction results for a II-VI MQW sample showing satellite peaks and thickness fringes that are characteristic of high quality material.⁶⁰

QC lasers are very complex MQW devices that required the convergence of molecular beam epitaxy growth technique and bandgap engineering for realization. In order to reliably fabricate this device, wave functions within the various section of the

structure must be modeled using a software program. To ensure accurate modeling, the material parameters such as the effective masses and the CBO must be known. Also, MQW structures with minimal thickness fluctuations and excellent interface quality are required. In the CER work done by Munoz et al, these critical material parameters were presented.²⁸ Lu et al was able to use this CER technique to design a structure for ISB absorption at 178 meV and confirm this using FTIR absorption spectroscopy (FTIR absorption at 180 meV).⁶⁰ Using HR-XRD Lu et al was able to demonstrate that device quality material can be grown.⁶² These studies provided the groundwork for the research presented in this thesis.

Chapter 5

Quantum Cascade Structure Design

Quantum cascade (QC) lasers are complex multi-quantum well (MQW) semiconductor structures in which the wave functions are engineered to ensure efficient electron injection and collection to and from the active region where infra-red (IR) light is emitted. This device consists of several active regions that are aligned as described in Fig. 5.1, to ensure the electron cascade effect when the structure is biased.

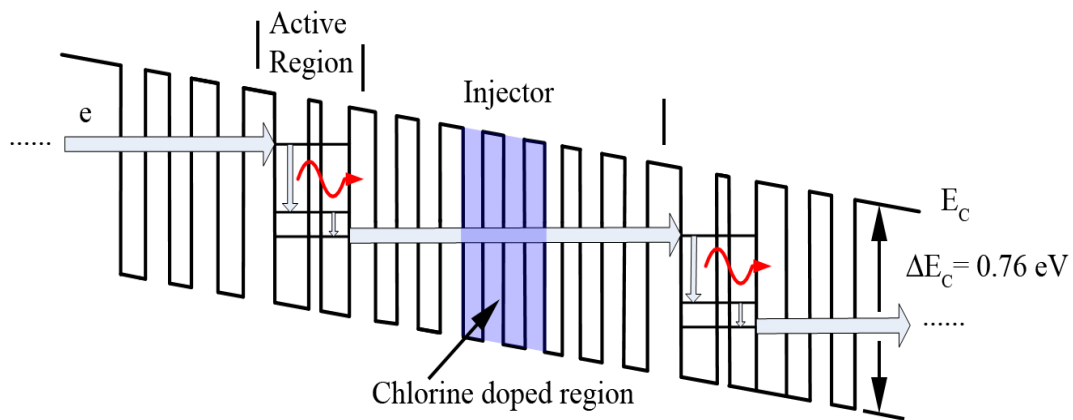


Figure 5.1: An illustration of the electron cascade effect as electrons flow through the biased laser core.

The active region must be designed to ensure light emission at a particular wavelength, minimize electron loss as a result of scattering and promote population inversion. As a first step in the research done for this dissertation, an electroluminescence (EL) structure was designed for emission at $4.5 \text{ }\mu\text{m}$. Given that this was the first attempt at a II-VI EL, structure every effort was made to keep things as simple as possible. The

active region of this simplified device was a two-well asymmetric couple quantum well (ACQW) designed so that the energy spacing between the upper and lower emission states ($e_3 - e_2$) is 276 meV (4.5 μm) and the energy separation between $e_2 - e_1$ is ~ 32 meV when an electric field of 67 KV/cm is applied. Before undertaking the complex growth, great attention was paid to proper modeling of the active region to ensure the energy level spacing is correct. This initial work would also give an insight to the accuracy of the growth and material parameters. To this end, a simple program base on the Schrödinger's equation and the transfer matrix technique was written to study unbiased active region.⁷⁰ After modeling the active region, an ACQW structure was grown and investigated with FTIR spectroscopy to ascertain compliance with the design.

5.1 Theoretical Background

In order to determine the wave function and energy level in the MQW structure, the Schrödinger's equation must be solved using boundary condition. The one dimensional Schrödinger's equation is as follows:

$$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \Psi(z,t) + V(z)\Psi(z,t) = j\hbar \frac{\partial}{\partial t} \Psi(z,t) \quad (5.1)$$

Here $\Psi(z,t)$ represents the wave function in space and time, $V(z)$ is the height of the barrier and m is the effective mass of the electron or hole. From this point m will represent the effective mass of the electron since attention will only be paid to the conduction band of the semiconductor. Equation (5.1) can be rewritten using the concept of separation of variables.⁷¹

$$\Psi(z, t) = \psi(z)\varphi(t) \quad (5.2)$$

Using equations (5.1) and (5.2) the Schrödinger's equation is presented as shown in (5.3)

$$-\frac{\hbar^2}{2m} \varphi(t) \frac{\partial^2 \psi(z)}{\partial z^2} + V(z) \psi(z) \varphi(t) = j\hbar \psi(z) \frac{\partial \varphi(t)}{\partial t} \quad (5.3)$$

Dividing both side of (5.3) by $\psi(z)\varphi(t)$ yields the Schrödinger's equation in which the variable are separated and is equal to the total energy of the particle E .

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(z)} \frac{\partial^2 \psi(z)}{\partial z^2} + V(z) = j\hbar \frac{1}{\varphi(t)} \frac{\partial \varphi(t)}{\partial t} = E \quad (5.4)$$

The time independent equation is generally be written as

$$\frac{\partial^2 \psi(z)}{\partial z^2} + \frac{2m}{\hbar^2} (E - V(z)) \psi(z) = 0 \quad (5.5)$$

while the time dependent part is expressed as $\frac{\partial \varphi(t)}{\partial t} = -\varphi(t)j\frac{E}{\hbar}$ where the solution is

$$\varphi(t) = \exp - j(E / \hbar)t \quad (5.6)$$

The general solution for the time independent Schrödinger's equation can be expressed as

$$\psi(z) = C_1 \exp(jkz) + C_2 \exp(-jkz) \quad (5.7)$$

$$\text{where } k = \sqrt{\frac{2m}{\hbar^2} (E - V(z))} \quad (5.8)$$

and C_1 and C_2 are constants. The effective mass of the electrons in the wells and barrier are a function of energy and can be represented as follows.⁷²

$$m_{\text{barrier}} = m_b(E = 0) [1 + (E - V(z)) / E_{BG}] \quad (5.9)$$

$$m_{\text{well}} = m_w(E = 0) [1 + (E - V(z)) / E_{BG}] \quad (5.10)$$

The semiconductor system that will be modeled is one where the barriers are finite (barrier = CBO) and it is assumed that $E \leq V(z)$ in that region. In the unbiased structure, the barrier is

$V(z) = \text{CBO}$ and k is a complex number, therefore the wave function is expected to decay exponentially as described by (5.11).

$$\psi(x) = A\exp(kz) + B\exp(-kz) \quad (5.11)$$

In the quantum wells where $V = 0$, the wave equation can be expressed as the sum of two orthogonal sinusoids:

$$\psi(z) = A\cos(kz) + B\sin(kz) \quad (5.12)$$

In order to solve this system, the follow must be assumed:⁷³

$$1) \int_{-\infty}^{\infty} |\psi(z)|^2 dx = 1 \quad (5.13)$$

2) $\psi(x)$ must be finite, single valued and continuous

3) $\frac{\partial \psi(z)}{\partial x}$ must be finite, single valued and continuous

5.2 Application of Boundary Conditions and the Use of the Transfer Matrix Technique

The ACQW active region that was studied in the initial stage of this research is shown in Fig. 5.2. The coefficients for the wave equation in wells and barriers will be solved by applying boundary conditions and making use of the transfer matrix technique.⁷⁰

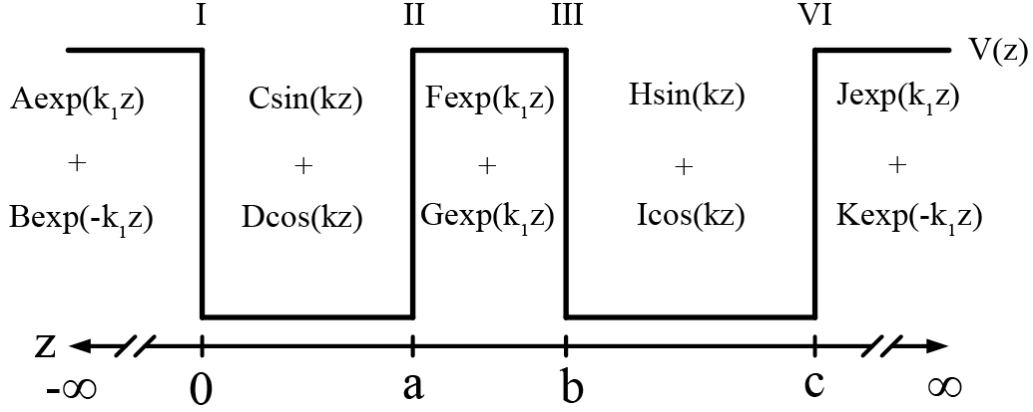


Figure. 5.2: Description of the asymmetric coupled quantum well system used for obtaining the energy states in the active region of the unbiased quantum cascade structure.

Boundary I: $A\exp(k_1 z) + B\exp(-kz) = C\sin(Kz) + D\cos(kz)$

$$\left. \begin{aligned} \psi(z)|_{z=0} : A + B &= D \\ \frac{\psi(z)}{\partial z}|_{z=0} : \frac{k_1}{m_b}(A - B) &= \frac{k}{m_w}C \end{aligned} \right\} \Rightarrow \overset{M_1}{\begin{pmatrix} 1 & 1 \\ \frac{k_1}{m_b} & -\frac{k_1}{m_b} \end{pmatrix}} \overset{M_2}{\begin{pmatrix} A \\ B \end{pmatrix}} = \overset{M_2}{\begin{pmatrix} 0 & 1 \\ \frac{k}{m_w} & 0 \end{pmatrix}} \overset{M_2}{\begin{pmatrix} C \\ D \end{pmatrix}}$$

Boundary II: $C\sin(Kz) + D\cos(kz) = F\exp(k_1 z) + G\exp(-k_1 z)$

$$\left. \begin{aligned} \psi(z)|_{z=a} : C\sin(ka) + D\cos(ka) &= F\exp(k_1 a) + G\exp(-k_1 a) \\ \frac{\psi(z)}{\partial z}|_{z=a} : \frac{k}{m_w}(C\cos(ka) - D\sin(ka)) &= \frac{k_1}{m_b}(F\exp(k_1 a) - G\exp(-k_1 a)) \end{aligned} \right\}$$

$$\Rightarrow \overset{M_3}{\begin{pmatrix} \sin(ka) & \cos(ka) \\ \frac{k}{m_w}\cos(ka) & -\frac{k}{m_w}\sin(ka) \end{pmatrix}} \overset{M_4}{\begin{pmatrix} C \\ D \end{pmatrix}} = \overset{M_4}{\begin{pmatrix} \exp(k_1 a) & \exp(-k_1 a) \\ \frac{k_1}{m_b}\exp(k_1 a) & -\frac{k_1}{m_b}\exp(k_1 a) \end{pmatrix}} \overset{M_4}{\begin{pmatrix} F \\ G \end{pmatrix}}$$

Boundary III: $F\exp(k_1 z) + G\exp(-kz) = H\sin(Kz) + I\cos(kz)$

$$\left. \begin{aligned} \psi(z)|_{z=b} : F\exp(k_1 b) + G\exp(-kb) &= H\sin(Kb) + I\cos(kb) \\ \frac{\psi(z)}{\partial z}|_{z=b} : \frac{k_1}{m_b}(F\exp(k_1 b) - G\exp(-kb)) &= \frac{k}{m_w}(H\cos(Kz) - I\sin(kz)) \end{aligned} \right\}$$

$$\Rightarrow \begin{matrix} M_5 \\ \begin{pmatrix} \exp(k_1 b) & \exp(-k_1 b) \\ \frac{k_1}{m_b}\exp(k_1 b) & -\frac{k_1}{m_b}\exp(k_1 b) \end{pmatrix} \end{matrix} \begin{pmatrix} F \\ G \end{pmatrix} = \begin{matrix} M_6 \\ \begin{pmatrix} \sin(kb) & \cos(kb) \\ \frac{k}{m_w}\cos(kb) & -\frac{k}{m_w}\sin(kb) \end{pmatrix} \end{matrix} \begin{pmatrix} H \\ I \end{pmatrix}$$

Boundary IV: $H\sin(Kz) + I\cos(kz) = J\exp(k_1 z) + K\exp(-k_1 z)$

$$\left. \begin{aligned} \psi(z)|_{z=c} : H\sin(kc) + I\cos(kc) &= J\exp(k_1 c) + K\exp(-k_1 c) \\ \frac{\psi(z)}{\partial z}|_{z=c} : \frac{k}{m_w}(H\cos(kc) - I\sin(kc)) &= \frac{k_1}{m_b}(J\exp(k_1 c) - K\exp(-k_1 c)) \end{aligned} \right\}$$

$$\Rightarrow \begin{matrix} M_7 \\ \begin{pmatrix} \sin(ka) & \cos(ka) \\ \frac{k}{m_w}\cos(ka) & -\frac{k}{m_w}\sin(ka) \end{pmatrix} \end{matrix} \begin{pmatrix} H \\ I \end{pmatrix} = \begin{matrix} M_8 \\ \begin{pmatrix} \exp(k_1 a) & \exp(-k_1 a) \\ \frac{k_1}{m_b}\exp(k_1 a) & -\frac{k_1}{m_b}\exp(k_1 a) \end{pmatrix} \end{matrix} \begin{pmatrix} J \\ K \end{pmatrix}$$

Now that the problem is transformed onto a matrix system, the coefficients can be found using a (5.14) as a starting point.

$$\begin{aligned} M_1 \begin{pmatrix} A \\ B \end{pmatrix} &= M_2 \begin{pmatrix} C \\ D \end{pmatrix} \\ M_3 \begin{pmatrix} C \\ D \end{pmatrix} &= M_4 \begin{pmatrix} F \\ G \end{pmatrix} \\ M_5 \begin{pmatrix} F \\ G \end{pmatrix} &= M_6 \begin{pmatrix} H \\ I \end{pmatrix} \\ M_7 \begin{pmatrix} H \\ I \end{pmatrix} &= M_8 \begin{pmatrix} J \\ K \end{pmatrix} \end{aligned}$$

This implies that

$$\begin{pmatrix} A \\ B \end{pmatrix} = M_1^{-1} M_2 M_3^{-1} M_4 M_5^{-1} M_6 M_7^{-1} M_8 \begin{pmatrix} J \\ K \end{pmatrix}. \quad (5.14)$$

Therefore the entire system can be expressed as a written using a 2 x 2 matrix

$$\begin{pmatrix} A \\ B \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} J \\ K \end{pmatrix} \quad (5.15)$$

$$\text{which can be rewritten as: } A = a_{11}J + a_{12}K \quad (5.16)$$

$$B = a_{21}J + a_{22}K \quad (5.17)$$

On inspecting the system in shown in Fig. 5.2 the coefficient $J = 0$ since the exponential term $J\exp(kz)$ approaches ∞ as $z \rightarrow +\infty$. Likewise coefficient $B = 0$ since $B\exp(-kz)$ approaches ∞ as $z \rightarrow -\infty$. Therefore (5.16) and (5.17) can be reduced to

$$A = a_{12}K \quad (5.18)$$

$$0 = a_{22}K \quad (5.19)$$

where $a_{12}(E)$ and $a_{22}(E)$ are both functions of the energy in the system.

To find the value of the unknown coefficients, first, the energy values that satisfy (5.19) were found. These energy value were then used to find the values of A , using (5.18).

Moreover, in order to find an expression for the wave function $\psi_i(z)$ corresponding to a given energy level E_i , the complete set of coefficients must be found iteratively starting with the coefficient A_i . This system was solved using a Matlab based program. First a program was written to generate a plot from which the energy values are extracted. These energy values are then place in the second program to plot the modulus square of the wave function. This program can easily be modified to model active regions with several quantum wells. See appendix A for the first designed EL structure growth sheet and

appendix B for the Matlab program that was used to predict the energy level distribution in the unbiased active region.

Chapter 6

The study of $\text{Zn}_{x'}\text{Cd}_{(1-x')}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ Quantum Cascade Structures Using Asymmetric Coupled Quantum Well Test Structures

6.1 Introduction

QC lasers that operate in the mid-infrared region are of great interest to the research community because of their potential application in areas such as infrared (IR) imaging and free space telecommunications.⁴ With this technology, it is possible to produce very narrow linewidth IR sources that are tunable. As a result, QC lasers are ideal for chemical spectroscopy^{3,5} and hence could find applications in areas such as atmospheric pollution monitoring, medicine and the military.

Since the first demonstration of the QC laser in 1994,² there has been very significant progress in their design and fabrication. It is now possible to produce InGaAs/InAlAs lasers that operate at room temperature and deliver power in excess 500mW and 1W in cw and pulse mode, respectively, within the 5 - 13 μm band.⁷⁵⁻⁷⁷ However, efforts to produce high performance QC lasers in the 3 - 4 μm region with this material have not seen similar success. This is mainly due to fact that InGaAs/InAlAs lattice matched to InP has a CBO of 0.52 eV, which limits the emission wavelength to $\sim 4.3 \mu\text{m}$ (or 3.4 μm when strain compensation is used).^{9, 74} Therefore, in order to cover the 3 - 5 μm atmospheric window, a material system with a larger CBO must be found.

The leading alternative material candidates to date are the InAs/AlSb lattice matched to InAs substrates and InGaAs/AlAsSb on InP substrates with CBOs of 2.1 eV and 1.6 eV, respectively.^{74, 78} These materials are very promising because they possess a CBO that should permit emission in the entire mid-IR band. With these materials, QC lasers with emission in the vicinity of 3 μm have been reported by several authors.^{74,78,79} While it is possible to adequately cover the 3 - 5 μm range of the mid IR band with these materials, their performance is still not comparable to their InGaAs/InAlAs counterparts in the 5 - 13 μm range. In the case of InGaAs/AlAsSb, the lower performance may be due to the limitation of the effective CBO to 0.5 eV due to Γ -X inter-valley electron leakage.⁸⁰ Assuming that the photon energy of an efficient QC laser is limited to $\sim \Delta E_c/2$, a high performance QC laser with emission wavelengths in the 3 - 5 μm range cannot be achieved.⁷⁴ With the InAs/AlSb material system on the other hand, the Γ -L inter-valley scattering limits the effective CBO to 0.76 eV (see Fig. 6.2).^{79,81} Although in this case the CBO is large enough to produce QC lasers within the 3-5 μm range, the laser performance still leaves much to be desired. The shortcomings of this material system may in part be due to the low thermal conductance of the InAs substrate and the relatively low confinement factor of the available laser waveguide.^{79, 82, 83} Also the lack of a common ions could result in a rough interfaces.²⁶ Given these shortcomings of the antimonides, the II-VI material system $\text{Zn}_x\text{Cd}_{1-x}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}/\text{InP}$, with an effective CBO of 1.12 eV and the absence of Γ -X inter-valley electron scattering as illustrated in Fig. 6.1, could be a viable alternative for producing high performance QC lasers within the 3 - 5 μm atmospheric window.

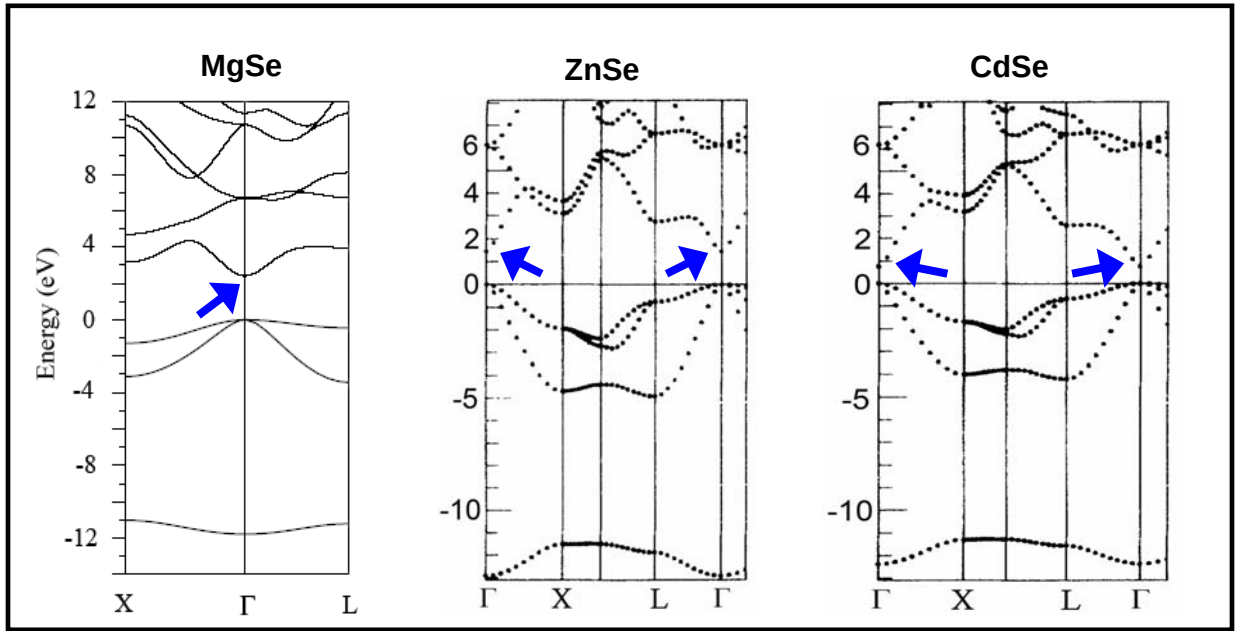


Figure 6.1: Wave functions within the first Brillouin zone of the II-VI binaries.⁸⁴ The blue arrows show the location of the Γ point. The X and L valleys are significantly higher than Γ therefore intervalley electron scattering should not be an issue.

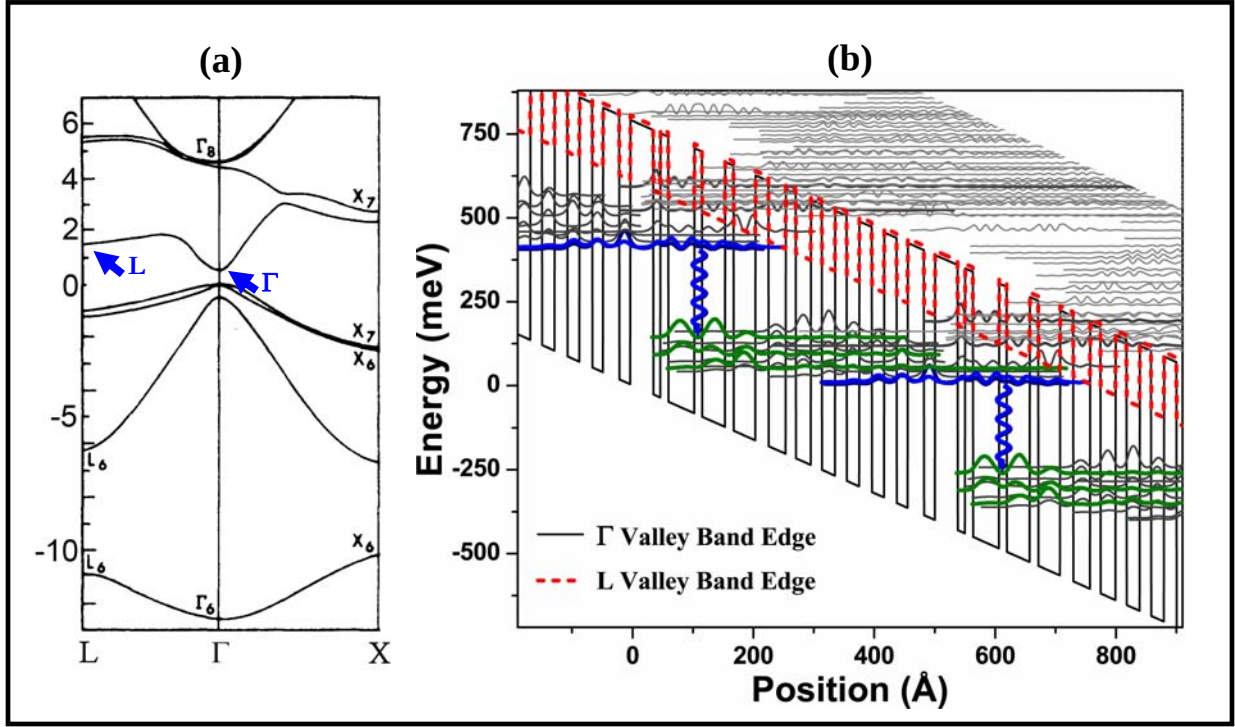


Figure 6.2: (a) Wave functions in the first Brillion zone of InAs.⁸⁵ (b) The conduction band profile for an antimonide based QC laser. The red dotted lines show the reduction in effective CBO due to Γ -L intervalley scattering in the InAs well material.

6.2 Experiment

In order to investigate the suitability of this material system for QC laser fabrication, an EL structure was designed for emission at 4.5 μm . In this design, the active region is composed of ACQWs separated by digitally graded superlattice injector regions. The central region of the injector is doped to increase electrical conductivity and reduce the incidence of space charge build up. Fig. 5.1 shows a schematic diagram of the EL structure. One period of the designed structure starting from the injection barrier is made up of the following layers in angstroms:

30/34/10/28/20/24/10/22/12/20/16/20/18/18/18/18/20/16/20/16/20/14/22/14/24/12/26/12

with the $\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ barrier indicated in bold and the Cl-doped layers underlined.

The ACQW region is shown in italics. This structure could be repeated 30 times to make up the EL structure. As can be seen, the growth of the EL structure is a very time consuming and complex process. In order to understand its properties, the material quality and energy level distribution within the active region must be assessed and well established. To do this, a structure made up of ACQWs equivalent to the active region of the EL structure, but separated by simple quaternary barrier layers rather than injector regions was grown.

6.3 MBE Growth

The ACQW structure was grown by molecular beam epitaxy (MBE) on (001) semi-insulating InP in a dual chamber Riber 2300P system. After deoxidation of the InP substrate in the III-V chamber, a 0.25 μm thick InGaAs buffer was grown at 400° C. The sample was then transferred via vacuum modules to the II-VI chamber where it was heated to 200° C. At this temperature, the InGaAs surface was exposed to a Zn flux for 40 s then a 10 nm ZnCdSe buffer layer was grown. At the end of this low temperature growth, the substrate temperature was raised to 300° C to complete the growth of the II-VI structure.⁶⁰



Figure 6.3: Ribier 2300P dual chamber MBE system used for growing II-VI QC structures.

One period of the ACQW structure starting from the spacer layer is made up of the following layers in angstroms: **190/34/10/28**. The barrier and spacer layers are shown in bold while the Cl-doped well layers are underlined. The ACQWs were repeated 25 times and the wells were doped with Chlorine ($n \sim 4 \times 10^{17} \text{ cm}^{-3}$) in order to observe intersubband (ISB) absorption during Fourier transform IR (FTIR) spectroscopy. The multiple ACQW structure was terminated with the growth of a 190 Å ZnCdSe cap layer. In order to ascertain the growth conditions that would provide the desired doping levels within the II-VI structure and determine the composition of the well and barrier layers, several calibration samples were grown. In order to determine the growth rate of the well and barrier material, bulk samples were grown and their thicknesses were measure using

SEM. The growth rate of the well and barrier were 0.4 and 0.9 $\mu\text{m/h}$, respectively. The carrier concentration of the doped calibration samples was assessed using Hall effect measurements. Through the use of PL and x-ray, the composition of the well and barrier (or spacer) were determined to be $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}$ and $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$, respectively. The barrier and well were designed to have a bandgaps of 3.03 and 2.08 eV at 300° C. With this material composition, the effective CBO was estimated to be 0.76 eV which is comparable to the effective CBO of InAs/AlSb when Γ -L electron scattering is taken into account.

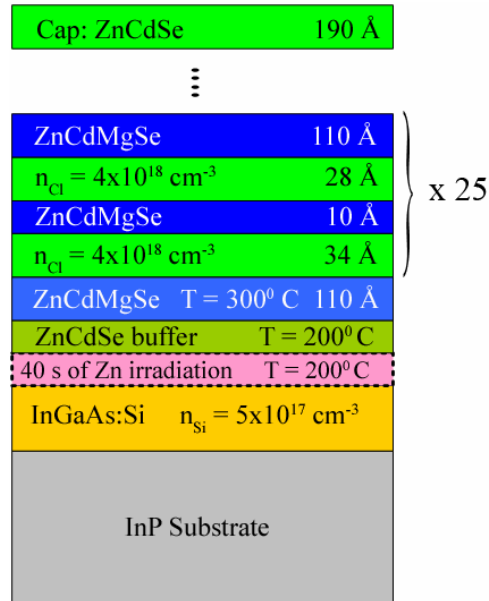


Figure 6.4: Description of an ACQW test sample grown to investigate the energy level distribution in the II-VI material system.

6.4 Results and Discussion

In order to determine the material quality of the ACQW structure, the sample was analyzed using photoluminescence (PL) and high resolution x-ray diffraction (HRXRD).

The large number of satellite peaks in the HRXRD curve, shown in Fig. 6.5, indicates that the structure is of excellent material quality. Using the satellite peaks separation (δ) the thickness of one period of the structure was calculated to be 270 Å which is in good agreement with the nominal value of 262 Å. This further indicates that there is good control of the well/barrier thickness. The absence of deep levels and the narrow linewidths of the PL spectra (67 meV at 300° K and 29 meV at 77° K) shown in Fig. 6.6 also indicate that the well/barrier interface is indeed good. To determine the energy level distribution within the ACQW structure the sample was polished into a waveguide with 45 ° facets and analyzed using FTIR absorption spectroscopy.

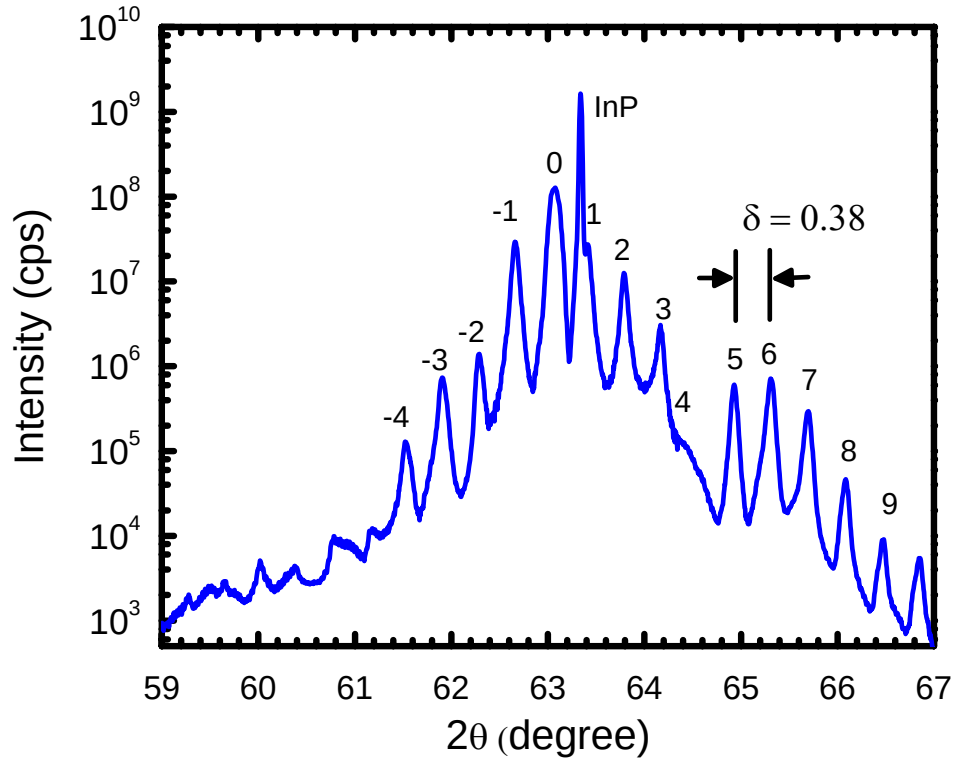


Figure 6.5: High resolution x-ray diffraction curve for 25 repeats of a $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}/\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$ ACQW structure.

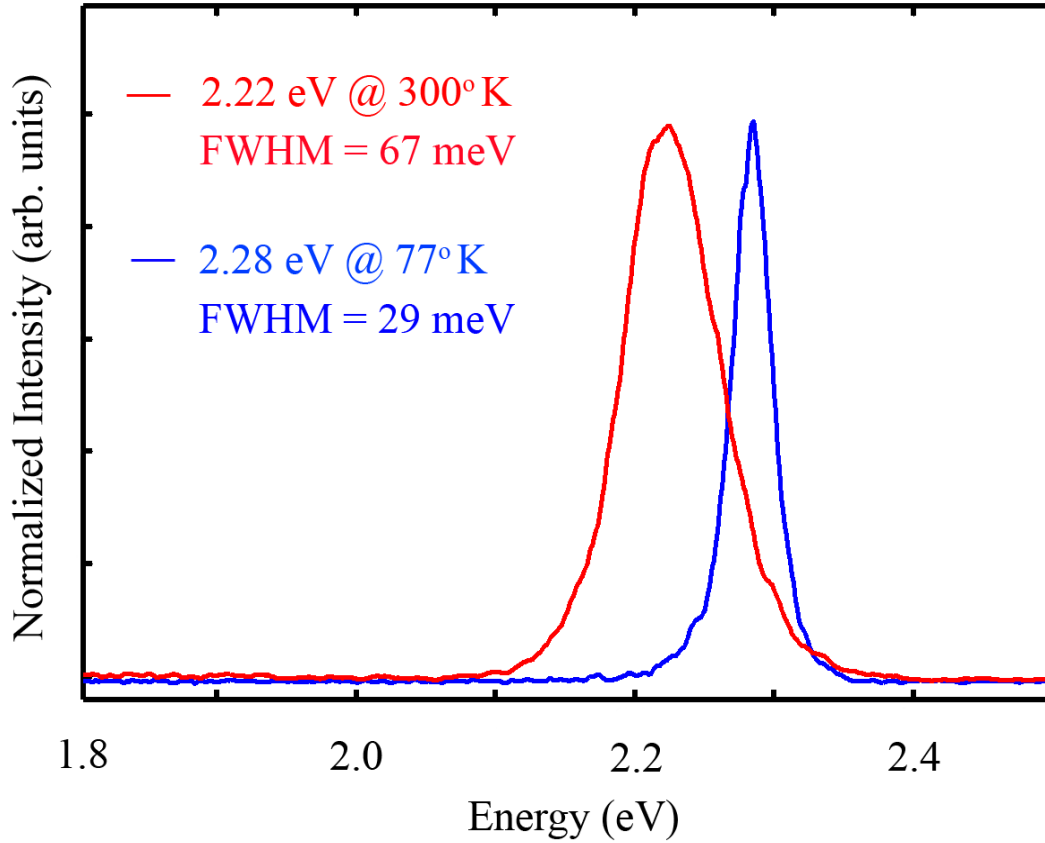


Figure 6.6: Photoluminescence spectrum for the ACQW structure of Fig. 6.5. The FWHM at 300 and 77 °K indicates that the material quality is very good.

The emission energy is in very close agreement with that predicted by simulations. During the FTIR measurements the IR light from the Nexus 670 light source, was focused onto the sample using a ZnSe lens. The transmitted light for the waveguide was then focused onto an external mercury cadmium telluride (MCT) detector. The results displayed in Fig. 6.7 suggest that the $\mathbf{e}_1 - \mathbf{e}_3$ and $\mathbf{e}_2 - \mathbf{e}_3$ absorption peaks occur at $\lambda = 4.13 \mu\text{m}$ and $\lambda = 5.18 \mu\text{m}$ corresponding to transitions energies 0.301 eV and 0.240 eV, respectively. This data indicates that the emission wavelength ($\mathbf{e}_2 - \mathbf{e}_3$) of the EL Structure grown with these active regions would be at about $5 \mu\text{m}$.

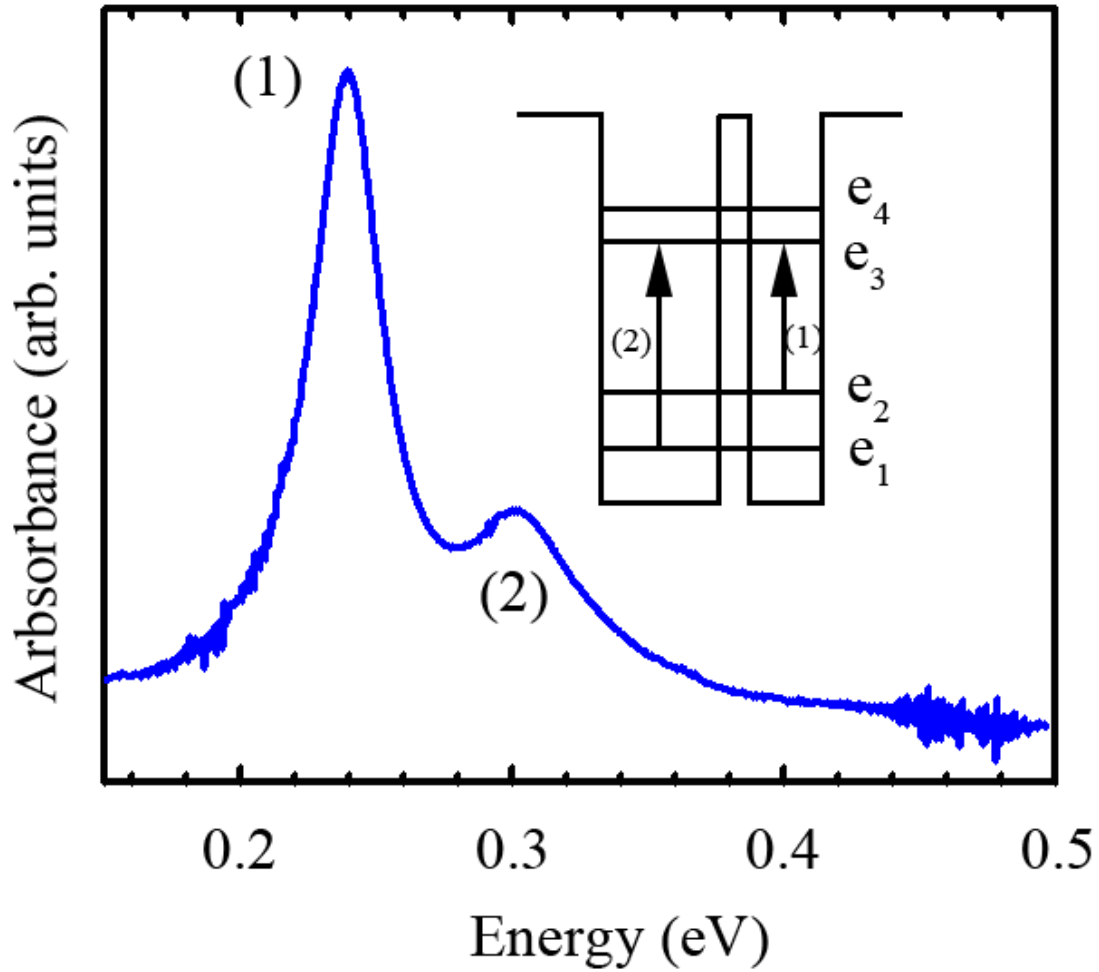


Figure 6.7: FTIR spectrum for the ACQW structure described in Fig. 6.4. The inset in the figure shows the electron transitions that produced the two peaks. The FTIR results suggest that: (1) $\mathbf{e1 - e3} = 0.301 \text{ eV}$ or $\lambda = 4.13 \text{ }\mu\text{m}$, (2) $\mathbf{e2 - e3} = 0.240 \text{ eV}$ or $\lambda = 5.18 \text{ }\mu\text{m}$.

A simulation based on the envelope function approximation was performed to determine the room temperature energy level distribution within the ACQW structure. The calculated $\mathbf{e1}$, $\mathbf{e2}$, and $\mathbf{e3}$ energy levels are 0.124, 0.171, and 0.437, respectively. Using this information, a comparison was made between the predicted and the measured transitions, and they are shown in Table 6.1.

Energy distribution	Predicted Energy (eV)	Measured Energy (eV)
PL ($\mathbf{e}_1 - \mathbf{hh}_1$)	2.230	2.210
$\mathbf{e}_1 - \mathbf{e}_3$	0.313 ($\lambda = 3.97 \mu\text{m}$)	0.301 ($\lambda = 4.13 \mu\text{m}$)
$\mathbf{e}_2 - \mathbf{e}_3$	0.266 ($\lambda = 4.67 \mu\text{m}$)	0.240 ($\lambda = 5.18 \mu\text{m}$)
$\mathbf{e}_1 - \mathbf{e}_2$	0.047	0.061*
*Inferred from the two measured FTIR peaks		

Table 6.1: Comparison between the calculated and measured energy transitions for the ACQW structure.

A good agreement between the predicted values and the measured values can be seen. From the FTIR results the separation between $\mathbf{e}_1$ and $\mathbf{e}_2$ was calculated to be 0.061 eV. Although this is larger than the design value of design value of 0.047 eV, it is within the calibration limits of our MBE system. It is expected that during device operation, this value will be reduced to the desired separation of ~ 32 meV (~ 1 LO phonon) when the complex injection barriers of the EL structure are used and a bias voltage is applied. A separation between $\mathbf{e}_1$ and $\mathbf{e}_2$ of ~ 1 LO phonon will ensure that population inversion between levels 2 and 3 will be achieved in a QC laser structure.

6.5 Summary/Conclusion

In conclusion, the FTIR results shown in Table 1 together with the PL and HRXRD analysis confirm that high quality ACQWs can be grown and used as test samples to analyze the design and optical characteristics of proposed QC laser structures before the complex and time consuming device growth is undertaken. We have also shown that

using the design parameters of the ACQW structure grown here, we should expect to fabricate an EL structure that emits at $\sim 5\text{ }\mu\text{m}$. To achieve shorter wavelengths an optimized design of the active region will be needed.

Chapter 7

Molecular Beam Epitaxy Growth and Electroluminescence of Optimized $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se-InP}$ Quantum Cascade Structures

7.1 Introduction

Recently, there has been great success in the production of mid-infrared QC lasers using the InGaAs/InAlAs-InP materials system that emits light in the 4 to 24 μm region.^{76,86-88} Within this wavelength range, the technology has progressed to the point where QC lasers are now finding commercial applications. These lasers can be made to operate in the absence of cryogenic cooling, allowing them to be part of very portable gas sensing instruments and infrared transmitters. Due to the high output power, tunability, and narrow linewidth of their emission, these devices are ideally suited for commercial applications in the areas of chemical spectroscopy and high-speed free-space telecommunication.^{4,5,89} However, research for QC structures operating below 4 μm using InGaAs/InAlAs has not had similar success because of the limited CBO of this material system.^{74,78} This limitation has led to the exploration of alternative materials.^{16,93}

With CBOs of 2.1 and 1.6 eV, several authors have reported QC laser emission as low as 3.0 μm using InAs/AlSb on InAs and InGaAs/AlAsSb on InP.^{16,74,78} However, the performance of the Sb-based devices is still not comparable to their InGaAs/InAlAs counterparts at longer wavelengths. This is in part due to the limitation of the effective CBO of InAs/AlSb and InGaAs/AlAsSb to about 0.76 and 0.5 eV, respectively, due to

inter-valley electron scattering.^{16,79-81} Also, in the case of the InAs/AlSb devices, low optical confinement factor (~52%) and growth related issues may be some of the reasons for their limited performance.^{16,26}

With an absence of intervalley electron scattering and an effective CBO of 1.12 eV (Ref. 29), the II-VI materials system is a very promising candidate for producing high performance QC lasers emitting below 4 μm . This chapter provides details on the MBE growth of the II-VI materials and multilayered structures. FTIR, PL and HRXRD data will be provided to show that device quality material can be grown with a high degree of thickness precision. The processing details for II-VI quantum cascade emitters will be provided together with the electroluminescence results. Comparisons will be made between the results obtained for ACQW test samples and QC emitter to show that very simple test sample can be grown to predict the optical properties of QC structures.

7.2 Experiment

In order to investigate the $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se-InP}$ suitability for QC laser fabrication, a QC emitter structure consisting of several hundred layers of alternating $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}$ and $\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ with precise thicknesses and compositions was designed to emit light at a wavelength of 4.5 μm . Several calibration samples were grown to determine the growth conditions for producing lattice matched $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}$ and $\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ layers and quantum wells with a CBO of ~0.80 eV. Calibration layers doped n-type with ZnCl_2 were also grown and Hall effect measurements were made to determine the carrier concentrations in the III-V and II-VI epitaxial layers that are needed for the device structures.

Based on these calibration runs, the material compositions for the II-VI epitaxial layers were selected to be $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}$ and $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$. These compositions produce ternary and quaternary layers lattice-matched to InP with bandgaps of 2.08 and 3.03 eV at 300 K, respectively, and are expected to have a CBO of 0.78 eV.⁹¹ The QC emitter was designed using a program that utilizes the envelope function approximation assuming an electron effective mass of $m_0 \times 0.128$ and $m_0 \times 0.181$ (where m_0 is the free electron mass) for $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}$ and $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$, respectively.²⁸ The simulation results showing the squared moduli of the wave functions in the conduction band is displayed in Fig. 7.1.

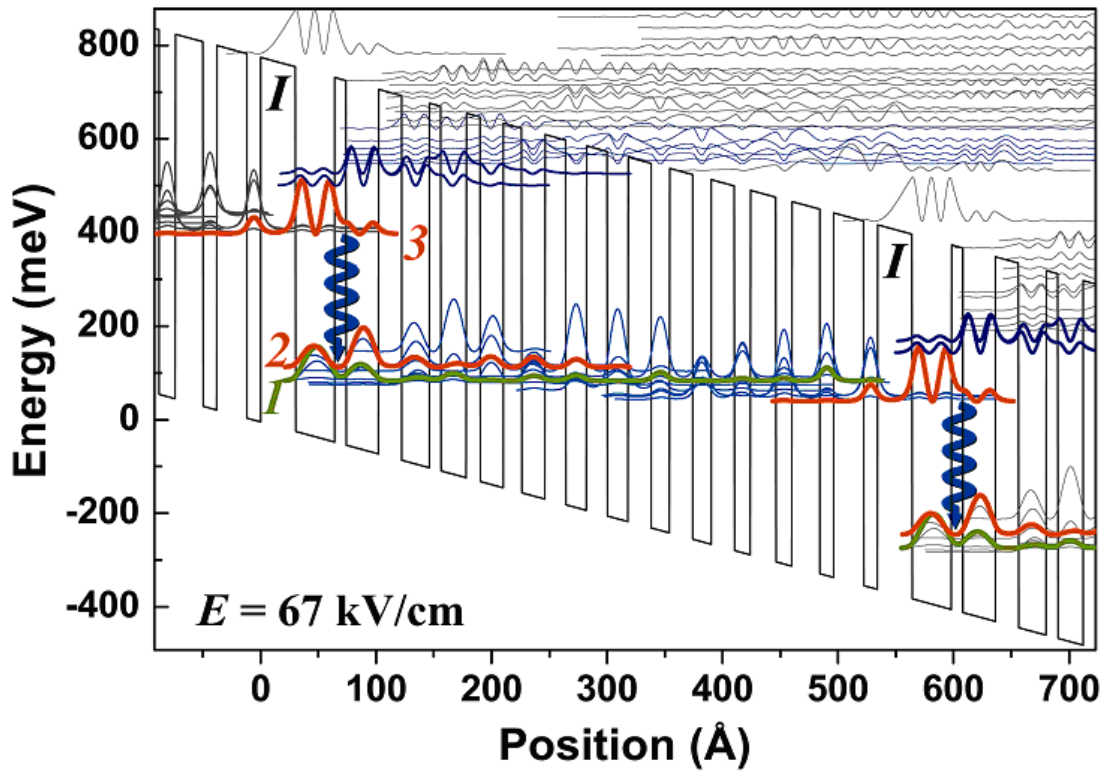


Figure 7.1: Simulation of the band structure of the QC emitter structure showing the modulus square of the wave function within the active/injector regions. ‘I’ denotes the injection barrier at the start of one active/injector period.⁹⁰

The proposed structure is composed of 20-30 repeats of the ACQW active regions with alternating (multi-layer) injector regions. One period of the designed structure starting from the injection barrier is made up of the following layers in angstroms:

30/34/10/28/20/24/10/22/12/20/16/20/18/18/18/18/20/16/20/16/20/14/22/14/24/12/26/12

with the $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$ barrier indicated in bold and the Cl-doped layers underlined. The ACQW layers are shown in italics.

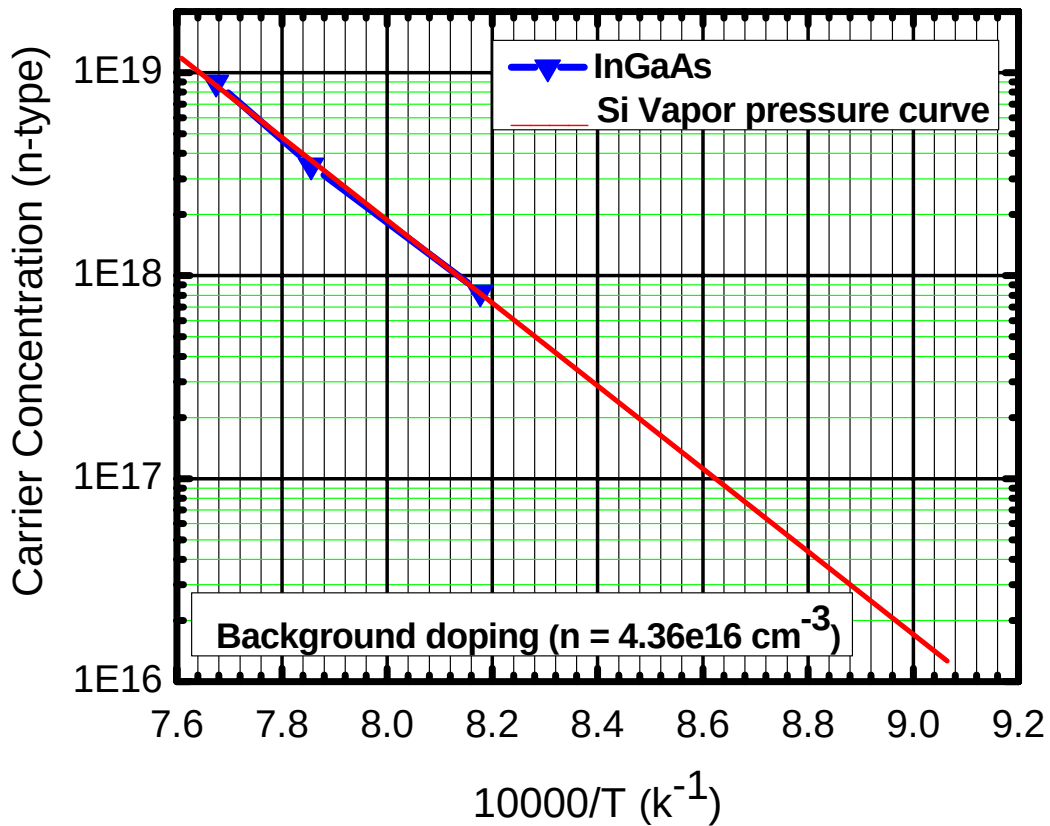


Figure 7.2: Carrier concentration for InGaAs grown at a rate of 0.8 $\mu\text{m/h}$. The carrier concentration of the calibration samples was obtained using Hall effect measurements.

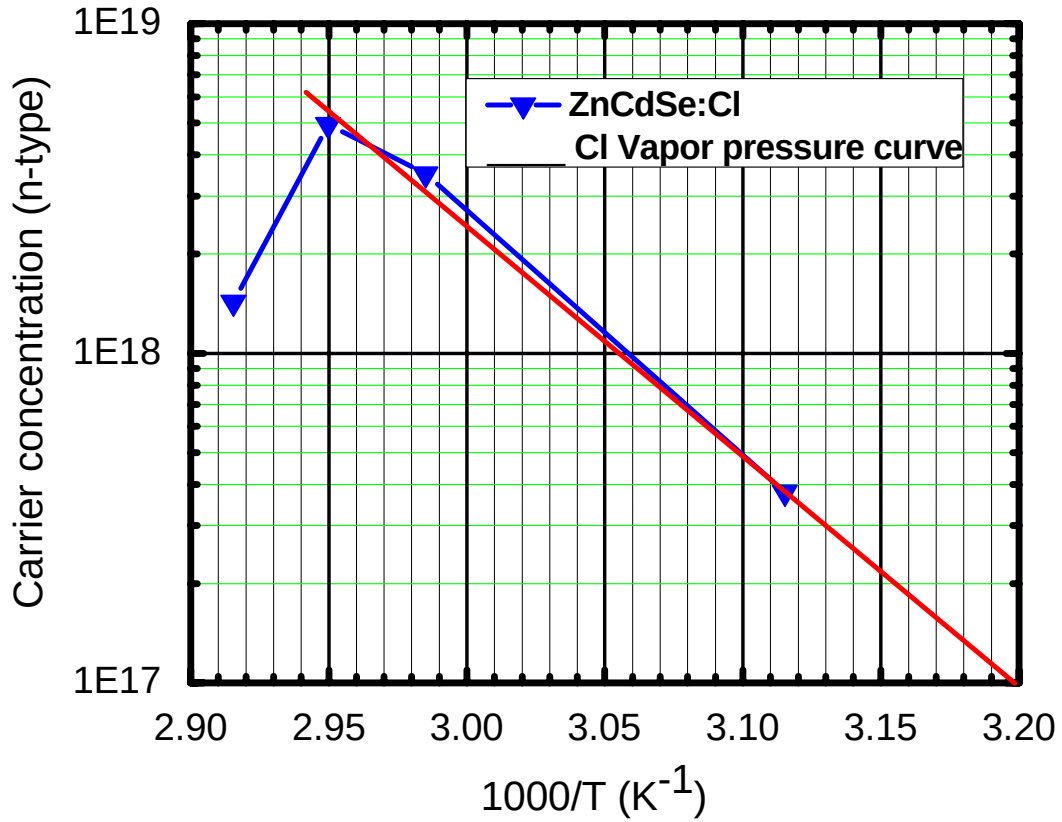


Figure 7.3: Carrier concentration for ZnCdSe grown at a rate of 0.3 $\mu\text{m/h}$. The carrier concentration of the calibration samples was obtained using Hall effect measurements.

In order to establish the accurate growth parameters that would lead to the growth of this complex multi-layered structure, another set of calibration samples composed of several repeats of the ACQW layers separated by simple quaternary barrier layers, rather than the multi-layered injector regions, were grown. The alternating ACQWs and quaternary barrier layers were repeated 25 times and the wells were doped with chlorine ($n \sim 4 \times 10^{18} \text{ cm}^{-3}$) to enable ISB absorption through multi-pass transmission experiments using FTIR absorption spectroscopy.⁹² Prior to the growth of the ACQW test structures,

individual layers were grown to determine the exact growth rate as well as the composition of the well and barrier materials used. Several samples were grown chlorine-doped for the purpose of calibrating the carrier concentration of the II-VI and III-V layers (see Figs. 7.2 and 7.3). In Chapter 6, the growth rates were determined by measuring the thickness of the II-VI epilayer using SEM and dividing by the growth time. The accuracy of the growth rate obtained using SEM is limited by the resolution of the SEM equipment and by your ability to accurately discern the interface between the III-V and II-VI layers. In this experiment, the growth rate of the II-VI materials were measured using RHEED intensity oscillations since this technique significantly improves the accuracy of the growth rate estimate.

7.3 MBE Growth

The structures were grown on (001) InP substrates by a solid source MBE system as described in Chapter 2. Before the growth of the II-VI layers, the InP substrate is heated in the III-V chamber under an arsenic overpressure until desorption of the oxide surface layer is achieved. The oxide desorption is assured by observing the transition from a (2x4) As-stabilized InP surface to the (4x2) In-stabilized InP surface. On observing this transition, the substrate temperature is rapidly lowered by 30° C before commencing growth of a lattice matched $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ buffer layer. The InGaAs buffer with a growth rate of 1 $\mu\text{m}/\text{h}$ is grown for 15 minutes under As-rich growth conditions at a substrate temperature that is 30° below the oxide layer desorption temperature. This 0.25 μm InGaAs buffer layer is grown to ensure that a smooth III-V surface with group-V termination is present for the initiation of the II-VI layer growth.

A sequence of steps has previously been developed to initiate ZnCdSe growth on an InGaAs surface.³³ Upon completion of the InGaAs layer growth, the sample is transferred to the II-VI chamber where the As-terminated InGaAs surface is exposed to a zinc flux for 40 s at a temperature of 200° C (Zn-irradiation). The Zn-irradiation step is performed to suppress the formation of In₂Se₃ and Ga₂Se₃ compounds at the III-V/II-VI interface. The presence of these selenium compounds must be minimized to prevent the formation of defects such as stacking faults which are known to degrade the material. This is followed by the growth of a low-temperature (200° C) Zn_{0.43}Cd_{0.57}Se buffer layer 90 s (~90 Å) to promote two-dimensional nucleation. It was previously shown that this sequence of steps, including the low temperature Zn_{0.43}Cd_{0.57}Se interfacial layer growth results in high quality epitaxy and reduces the defect densities to ~10⁴ cm⁻³.³² After the low temperature layer deposition, the growth is interrupted and the substrate temperature is raised and stabilized at 300° C under a selenium flux before resuming the growth of the II-VI structure. The growth rates of ZnCdSe and ZnCdMgSe were typically 0.30 and 0.85 μm/hour, respectively, and the Se/group-II flux ratio was maintained at above 4, ensuring Se-stabilized growth conditions. Measurement of the RHEED intensity oscillations was typically done after the growth interruption, at the initiation of the growth at 300 °C. The RHEED intensity oscillation traces, shown in Fig. 7.4 a and b, indicate a clear layer-by-layer growth mechanism during the growth of these materials, and enable us to establish the growth rates with high accuracy. After growth, the ACQW structure samples were analyzed using PL, HRXRD, and FTIR spectroscopy.

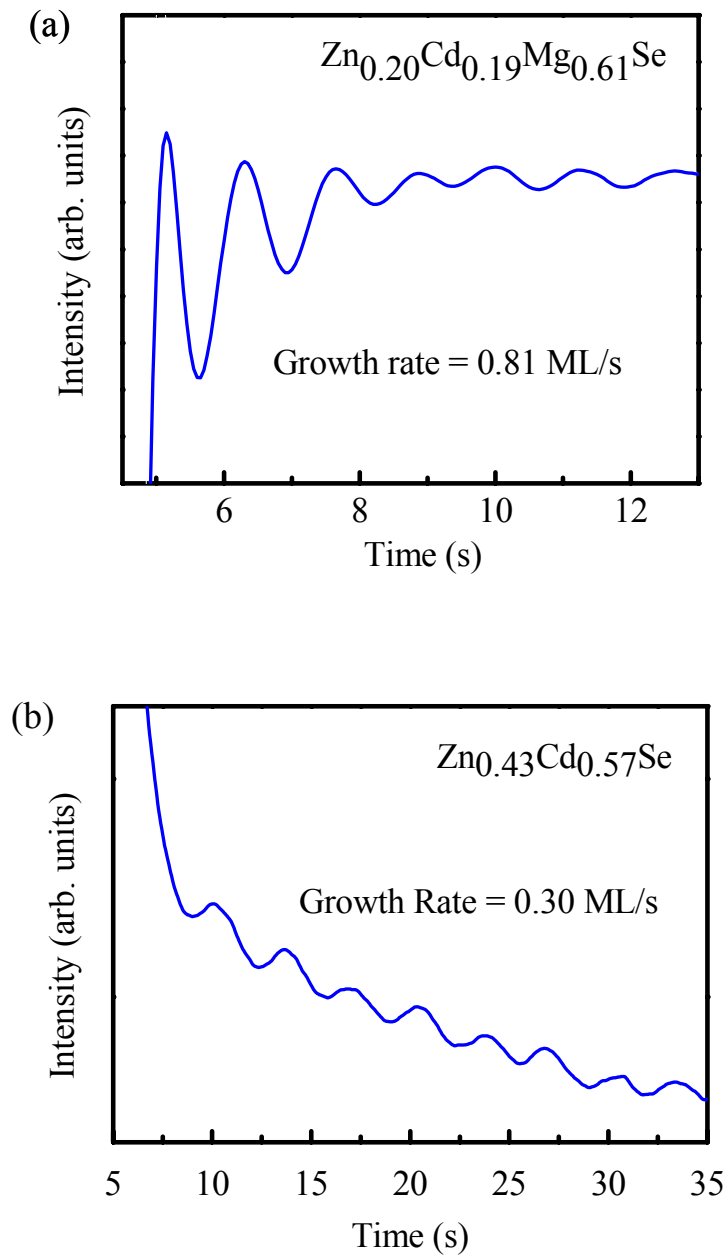


Figure 7.4: Traces of the RHEED intensity oscillations measured during growth of (a) $\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se}$ and (b) $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}$ calibration samples.

7.4 Results/Discussion

The room temperature FTIR absorption for the first ACQW structure grown is shown in Fig. 6.7. The two absorption peaks seen at 0.240 and 0.301 eV were assigned to the $\mathbf{e}_2 - \mathbf{e}_3$ and $\mathbf{e}_1 - \mathbf{e}_3$ transitions. Simulations based on the envelope function approximation, predict $\mathbf{e}_2 - \mathbf{e}_3$ and $\mathbf{e}_1 - \mathbf{e}_3$ absorption at 0.266 and 0.313 eV, respectively. Furthermore, a separation of $\mathbf{e}_2 - \mathbf{e}_1$ of 0.061 eV is deduced from the two FTIR peaks, while the predicted value based the simulation was 0.047 eV (Ref. 92). The combination of these energy discrepancies is consistent with the ACQW barrier being slightly thinner than intended. At this point, the growth was re-calibrated and a second ACQW structure was grown and characterized. For the re-calibration, we incorporated the use of RHEED intensity oscillations to improve the accuracy of the growth rates.

The layer sequence in angstroms for one period of the second ACQW structure is as follows; **110**/34/**10**/28 where the chlorine-doped well layers are underlined and the barrier (quaternary) layers are in bold. The nominal (design) thickness of one period of the structure is 182 Å. Using an average satellite spacing of $\delta 2\theta = 0.59^\circ$ obtained from the HRXRD plot shown in Fig. 7.5, the grown period thickness was calculated to be 176 Å, indicating very good control of the well/barrier thickness (~ 3% difference). The inset in Figure 7.5 shows an expanded view of the region near the zero-order peak. Clear interference fringes can be seen in the inset also indicating excellent material quality.

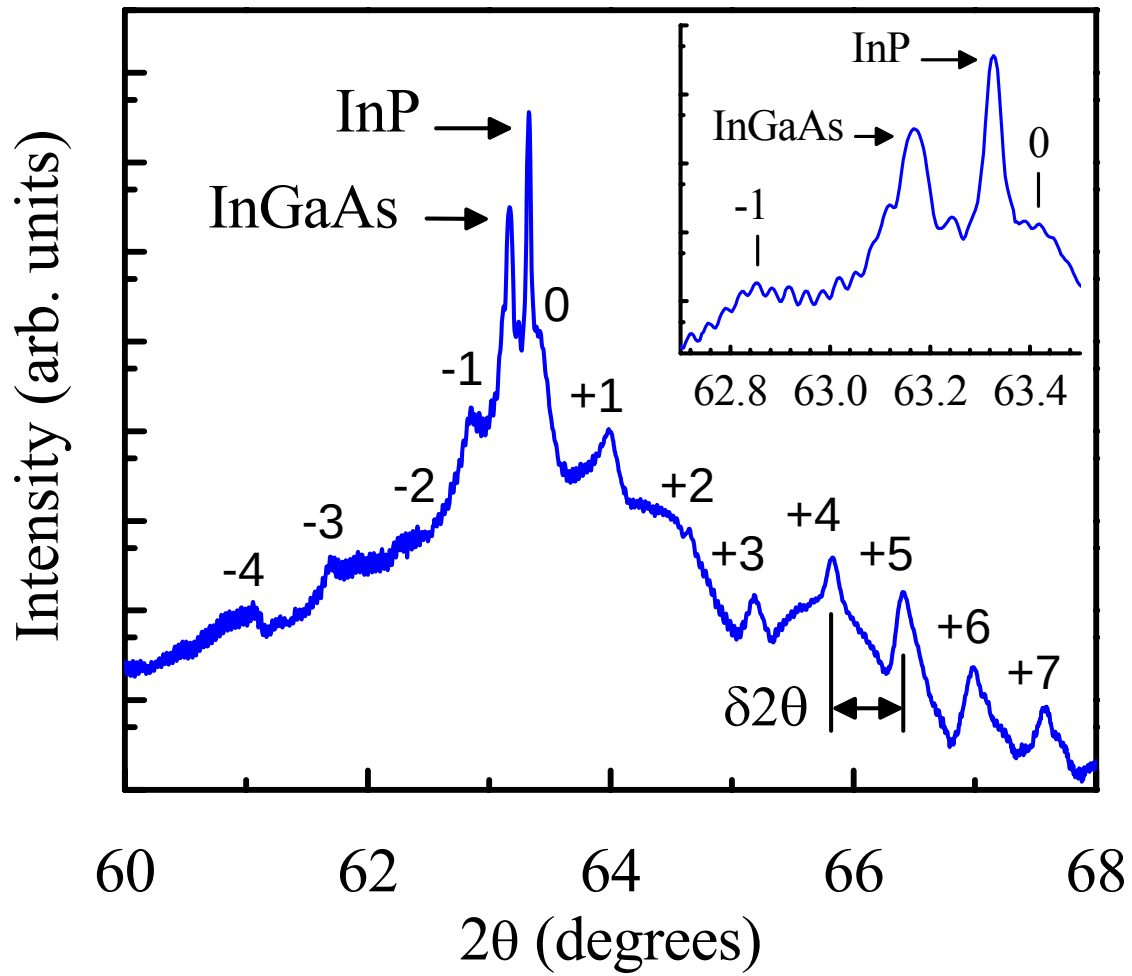


Figure 7.5: HRXRD spectra for the second ACQW structure plotted on a logarithmic scale. The inset is an expanded region around the zero-order peak showing the presence of thickness fringes, characteristic of very high quality material.

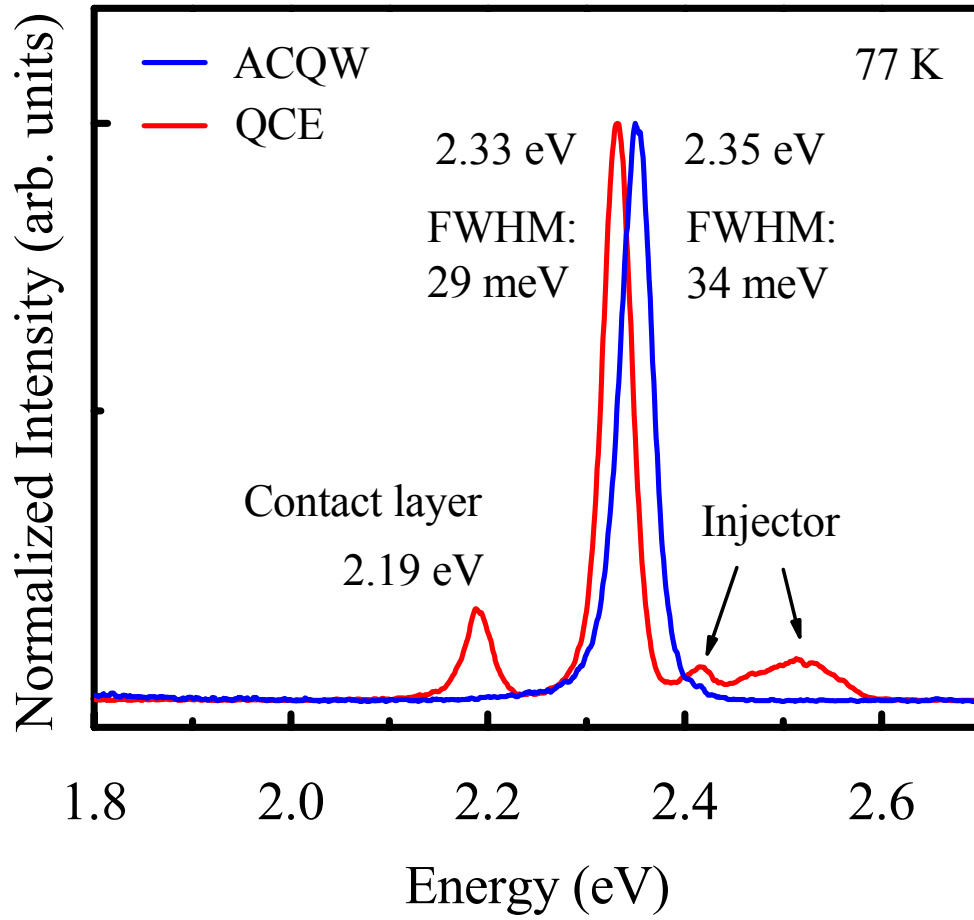


Figure 7.6: PL spectra at 77K for the second ACQW and the QC emitter structure.

This test sample was also investigated using PL and the results are shown in Fig. 7.6. The linewidth of the PL at 77 K was 34 meV. This narrow linewidth and the absence of deep levels in the PL spectrum confirm that the material and the well/barrier interface quality are good.

The second ACQW structure was processed into a waveguide with 45° facets for use in FTIR spectroscopy. The infrared light from the Nexus 670 FTIR spectrometer was allowed to pass through a polarizer which was used to resolve the light into its TM and TE components. The light that passed through the polarizer was then focused onto a 45° facet of the sample using a ZnSe lens. After making several bounces through the waveguide the light that emerged through the second facet was collected and focused onto a liquid-nitrogen cooled external mercury cadmium telluride (MCT) detector using another set of ZnSe lenses. The room temperature FTIR spectrum for the second ACQW structure is shown in Fig.7.7. The vertical lines represent the values predicted by the simulation for this ACQW structure. A comparison of the FTIR results obtained from the test sample and absorption peaks predicted by simulations is also displayed in Table 7.1

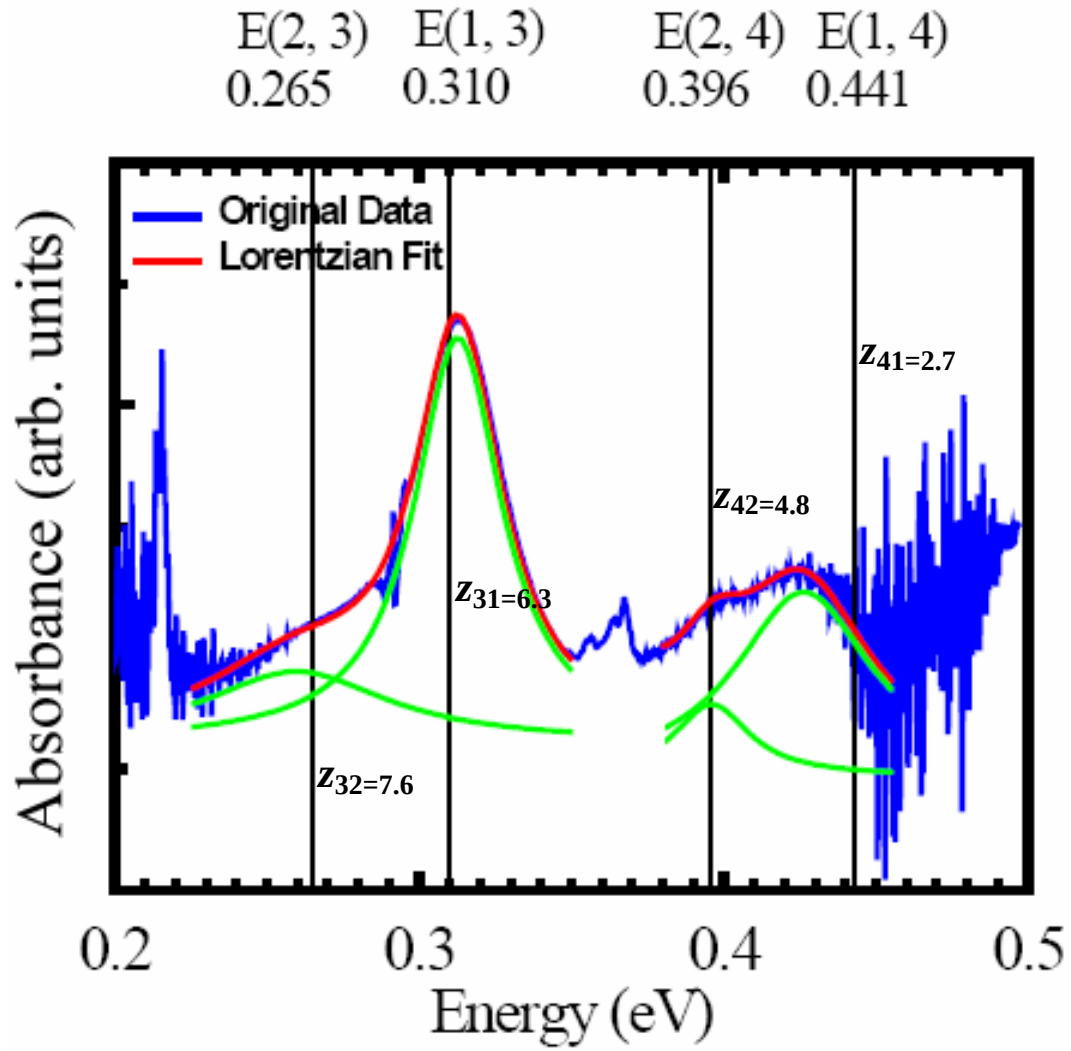


Figure 7.7: FTIR absorption spectra for the second ACQW at 300 K. The vertical lines represent the simulation results for the ACQW structure while the red and green lines represent the results for a Lorentzian fit.

Transition	Simulation (meV)	1st ACQW (meV)	2nd ACQW (meV)
E1 – E4	441	—	427
E2 – E4	396	—	397
E1 – E3	310	301	313
E2 – E3	265 (4.69 μm)	240 (5.18 μm)	261 (4.76 μm)
E1 – E2	45	61	52

Table 7.1: Comparison between simulation data and FTIR absorption results for two ACQW structure grown to study the active regions of II-VI QC structures. The growth rates for the 1st and 2nd ACQW structures were obtained from SEM and RHEED oscillation measurements, respectively.

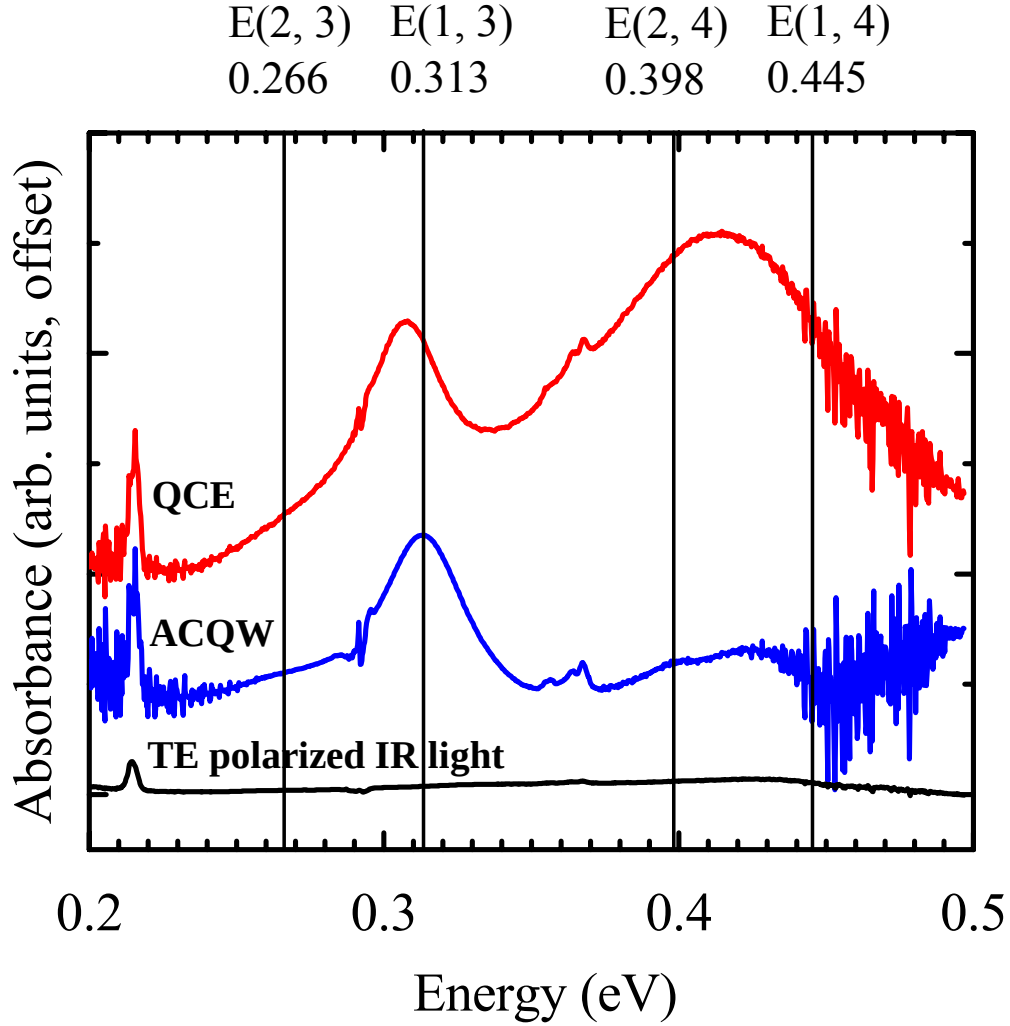


Figure 7.8: Comparison of room temperature FTIR results obtained from QC emitter and the optimized 2nd ACQW test sample.

Figures 7.6 and 7.8 also show, for comparison, the PL and FTIR absorption spectra for the QC structure that was grown according to these improved growth parameters.⁹⁰ The slight red shift in the QC structure's $\mathbf{e}_1 - \mathbf{e}_3$ FTIR absorption energy relative to the same transition in the ACQW structure is consistent with a reduction in the energy level

spacing expected when the thick quaternary barrier in the ACQW structure is replaced with a digital superlattice injector in the QC emitter structure. We tentatively identify the broad, higher energy absorption as originating from the $e_2 - e_4$ and $e_1 - e_4$ transitions present in the un-biased QC emitter structure. In addition to the dominant peak due to emission from the active region, the PL spectrum of the QC emitter exhibits emissions originating from the injector region and the contact layer. The presence of the superlattice injector regions in the QC structure is also responsible for the slight red shift of the dominant PL emission peak.

7.5 Device Processing and Electroluminescence Results

The EL samples were made into QC emitters using photolithography and electron beam metal contact deposition. To start the process, the II-VI material was processed into circular mesa structures using lithographically patterned 400 μm circles. These circles were then etched into mesas using $\text{HBr}:\text{HNO}_3:\text{H}_2\text{O}$ (1:1:10) wet chemical etch solution. This etch was allowed to proceed into the II-VI contact layer. Hydrogen Fluoride (HF) and O_2 was used to remove the photoresist and clean the semiconductor surface before a second lithography step was used for the application of metal contacts. The top contact consisted of 150 $\text{\AA}$ of Ti followed by 2500 $\text{\AA}$ of Au. The back of the sample was lapped before InP back-side contact was made using Ge/Au. At the end of this processing, the mesas were cleaved into semi-circular discs and indium soldered to a copper heat sink. The top contact metal contacts were wire bonded to contact pads.

(a)



(b)

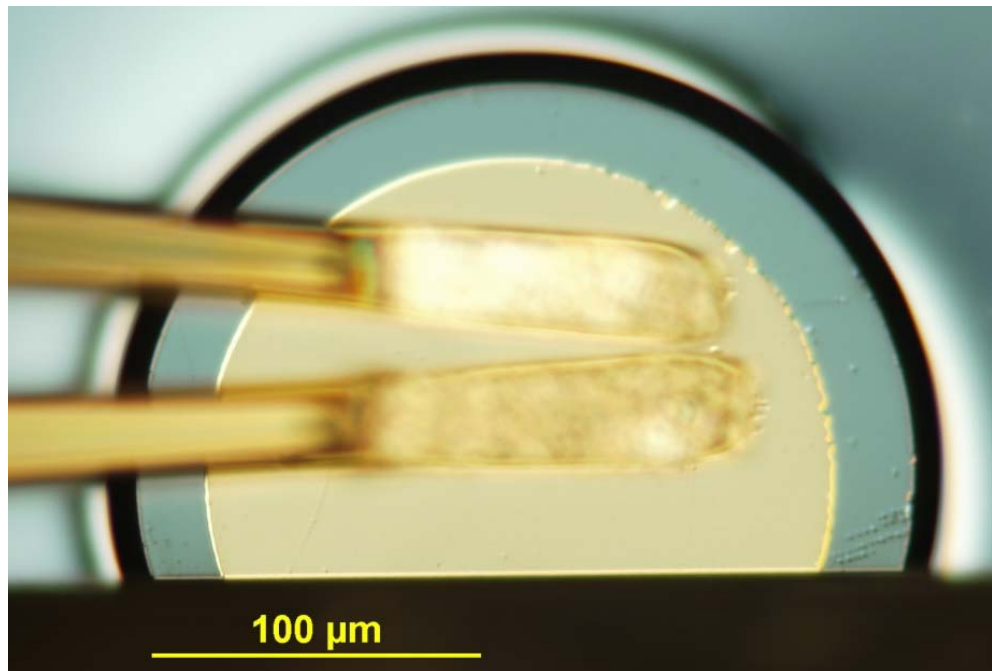


Figure 7.9: SEM image of the QC emitter. (a) Cross section of the cleaved mesa. (b) Top view showing bonded electrical contact.

Electroluminescence from a 0.036 mm^2 QC emitter heat-sunked to a copper plate was collected for drive currents ranging from 1.0 – 3.5 A using a FTIR spectrometer in step scan mode and a cooled MCT detector.⁹⁰ The LIV curve for the device at temperatures ranging for 78 – 300 K is shown in Fig. 7.9. These results are consistent with normal QC operation. The QC emitter electroluminescence, shown in Fig. 7.10, is centered at $4.8 \text{ }\mu\text{m}$, which is in excellent agreement with the design emission wavelength of $4.5 \text{ }\mu\text{m}$.

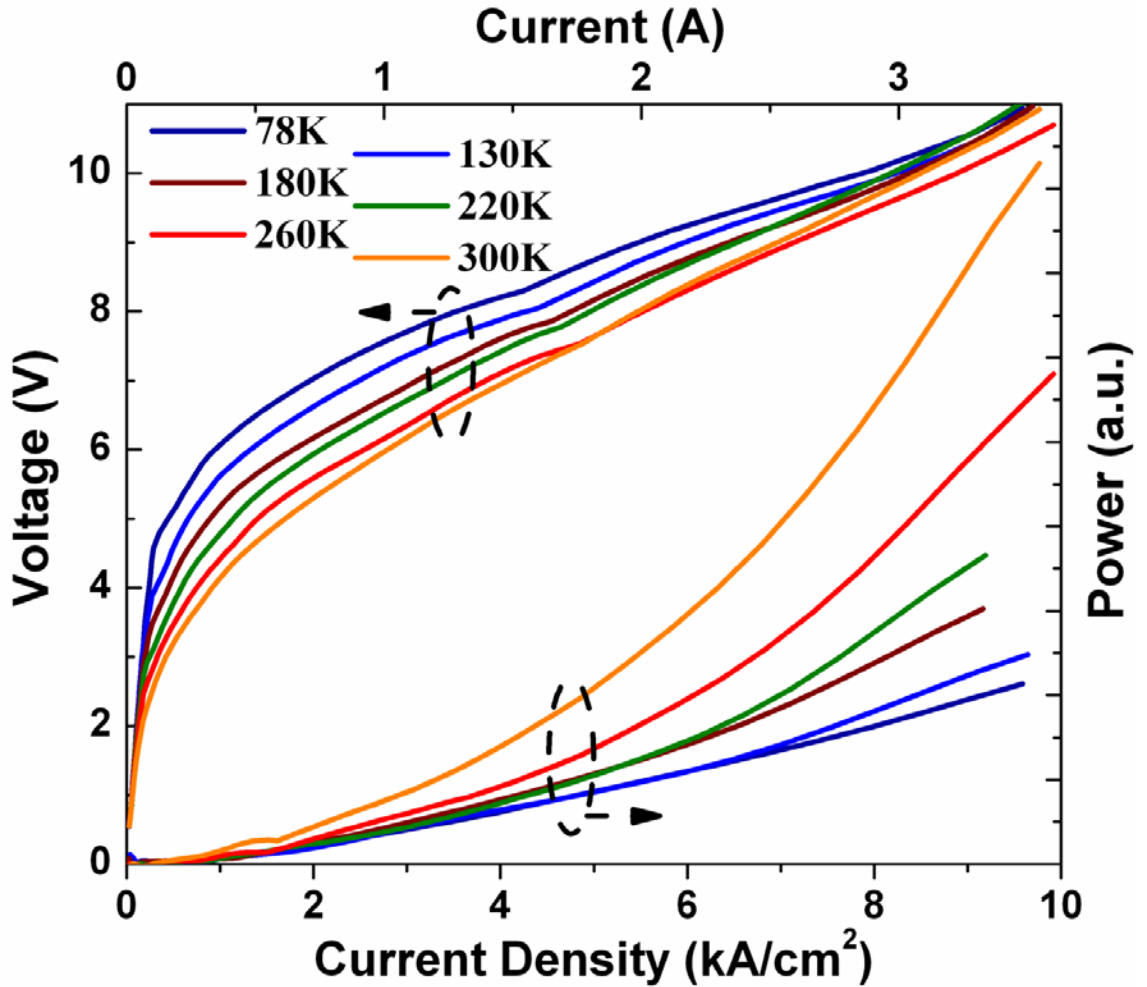


Figure 7.10: LIV curves for the II – VI electroluminescence structure heat-sunked at temperatures ranging for 78 – 300 K.

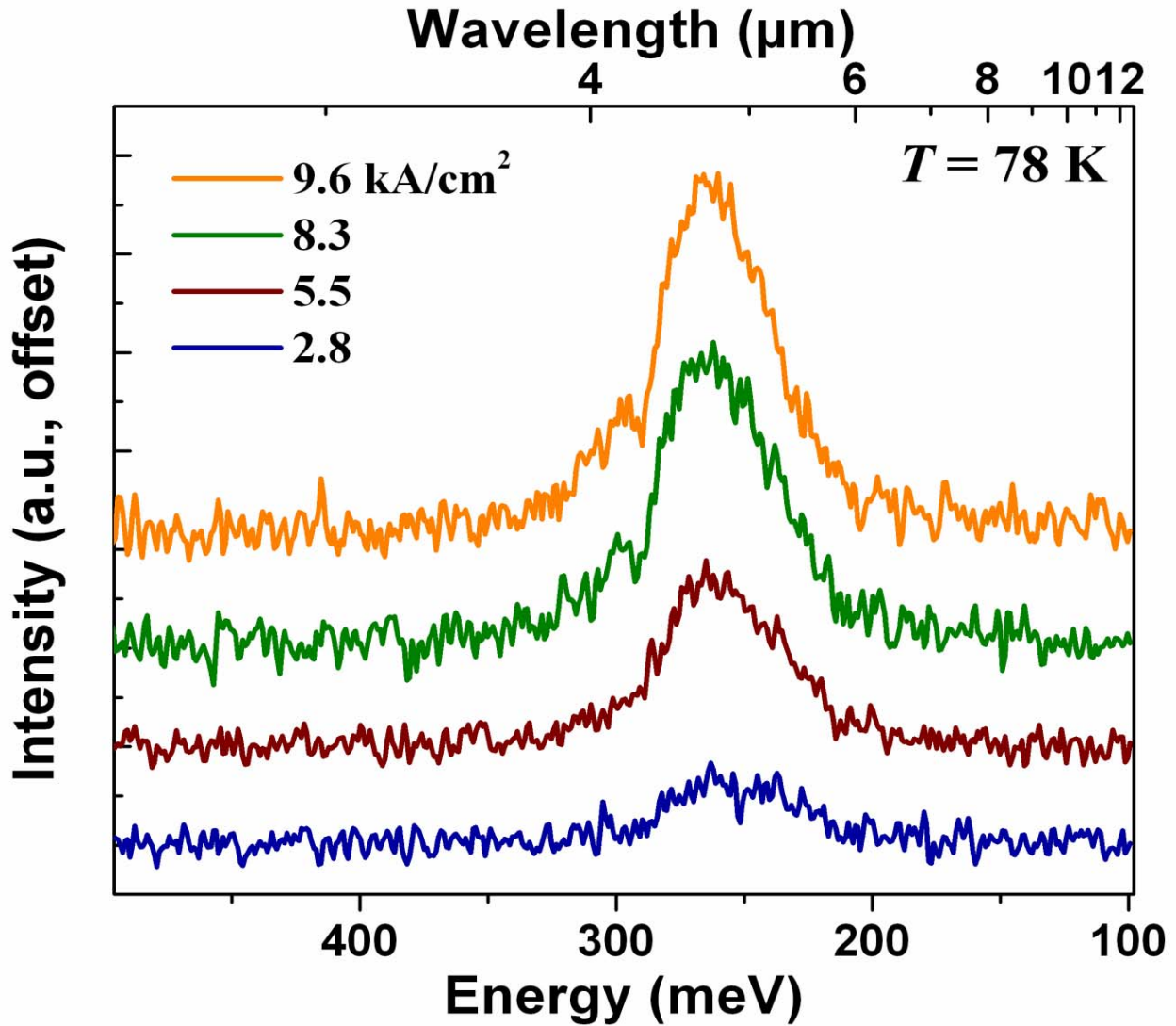


Figure 7.11: Electroluminescence results for a II-VI QC structure that was designed to emit at $4.5 \mu\text{m}$ (78 K).

A secondary peak emerged as the operating temperature of the device was increased (see Fig. 7.11). In order to ascertain the origins of this peak the emission was analyzed using a polarizer. At the end of this polarization study it was observed that all of the emission is transverse magnetic (TM) in nature (see Fig. 7.12). This suggests that all of the emission was due to ISB transition in the QC emitter and not due to black body radiation. The

secondary peak which is centered about 9.0 μm is consistent with the $\text{e4} - \text{e3}$ electronic transition.

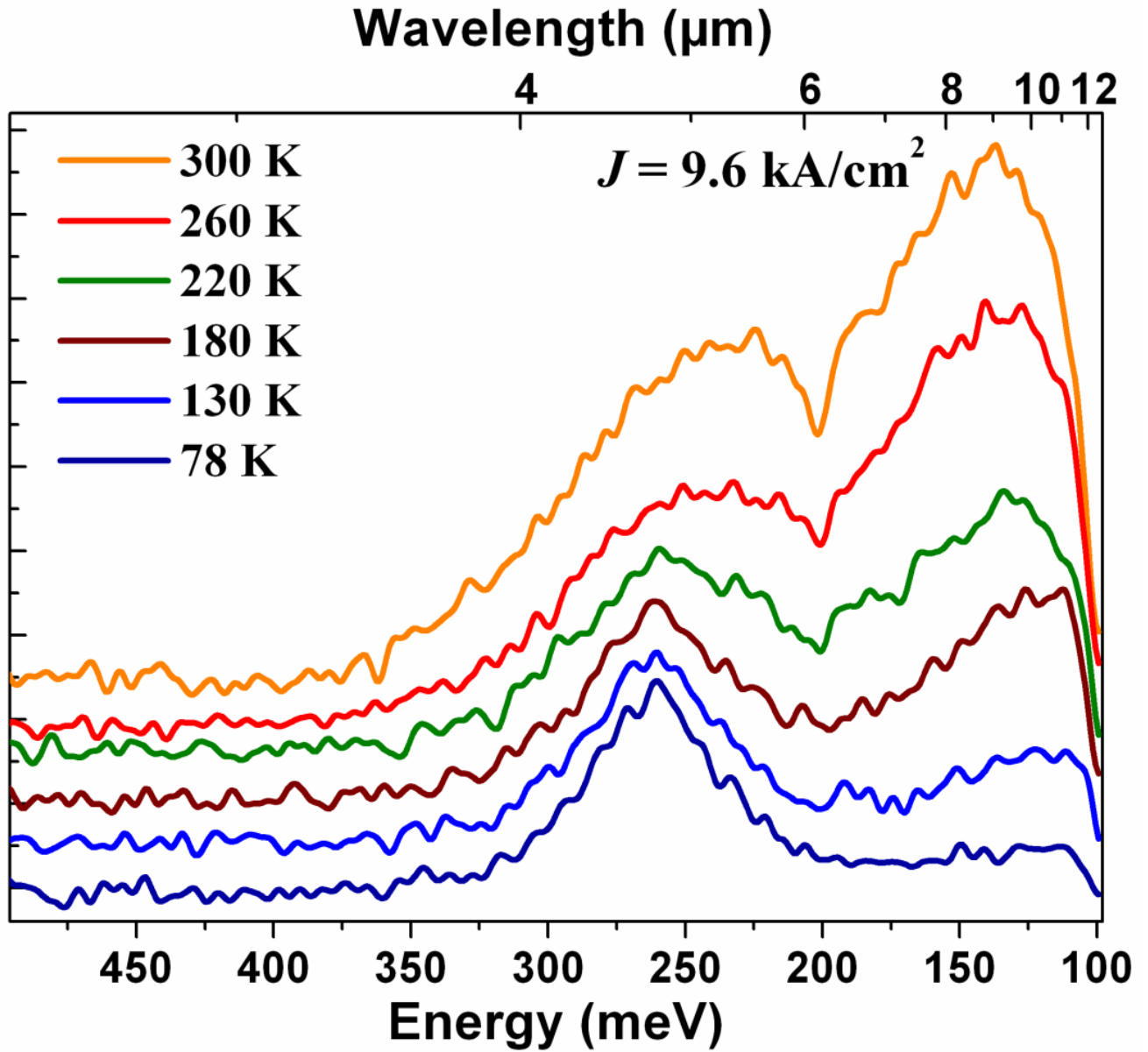


Figure 7.12: II – VI QC electroluminescence for device operating at a drive current of 3.5 A (9.6 kA/cm) over a temperature range of 78 – 300 K.

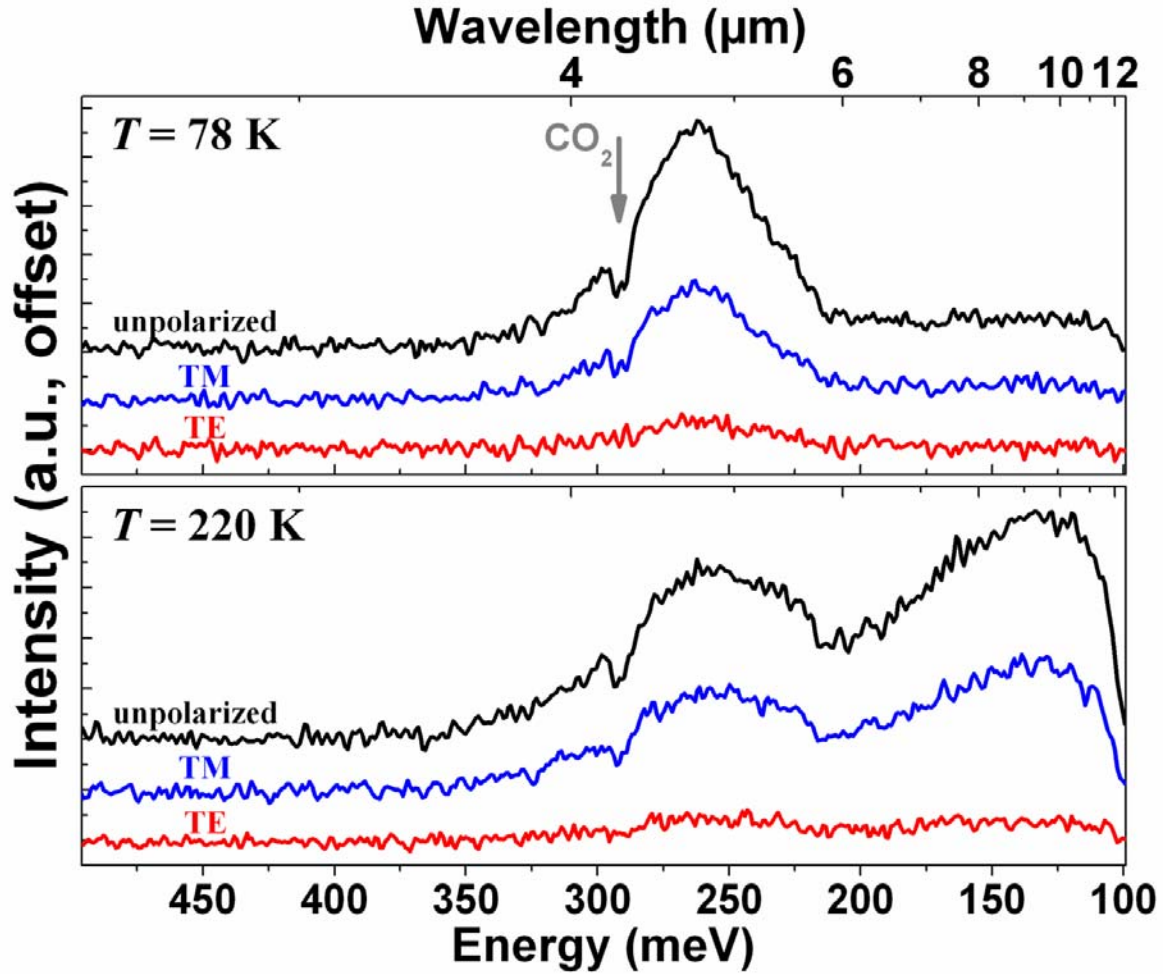


Figure 7.13: Result of polarization study of II – VI QC electroluminescence at 78 and 220 K.

7.6 Summary/Conclusion

In conclusion, a $\text{Zn}_{0.43}\text{Cd}_{0.57}\text{Se}/\text{Zn}_{0.20}\text{Cd}_{0.19}\text{Mg}_{0.61}\text{Se-InP}$ QC emitter was designed for emission at 4.5 μm . In order to establish the optimum growth parameters needed to achieve the appropriate energy level distribution in the active region of the QC structure, two ACQW test samples were grown and investigated. PL and HRXRD analysis of the test samples indicate that the multi-layers in this materials system can be grown with very

high quality and control. More specifically, the HRXRD shows that the well/barrier layer thickness can be controlled to within 3% of the desired value. After careful calibration of the growth parameters, including the use of RHEED intensity oscillation measurements to accurately establish the ternary and quaternary layer growth rates, FTIR results for the second ACQW and QC emitter structures were compared to simulation results. The measured FTIR peaks are in good agreement with the values predicted by the simulation. A QC emitter sample grown with these optimized conditions was processed and investigated for electroluminescence at 77 K. Emission was observed at 4.8 and 9.0 μm . The secondary peak at 9.0 μm increased in intensity with temperature. To rule out the possibility of black body radiation, a polarization study was performed. This polarization study proved that all observed peak were due to ISB transitions within the active region of the QC structure. Also, the observed emission at of 4.8 μm compares very well with the design value of 4.5 μm . These results demonstrate that the growth of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ on InP substrates by molecular beam epitaxy can be accurately controlled to provide the stringent layer thickness, composition control, and excellent material quality that are needed for these complex multi-layered device structures.

Chapter 8

Growth of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ -InP Quantum Cascade Structures with 3-well Active Region and Cladding Layers for Emission in the 3 – 5 μm Range

8.1 Introduction

The production of high performance QC lasers in the 3 to 4.0 μm range is still a challenge due to the limited CBO of the lattice matched InGaAs/InAlAs material that is commonly used to fabricate these devices.^{9,10} In order to overcome this problem, strain compensation has been explored as a means of increasing the CBO.⁹⁻¹¹ However, devices produced with strain compensation show non-optimum performance below 4.0 μm due to the presence of intervalley electron scattering. This has resulted in the exploration of other material systems with larger CBOs.^{16,74,78} In this chapter an alternative approach is presented in which the wide bandgap $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ -InP material, a II-VI material system, is used. This II-VI material system is very promising because type-I multi-quantum wells structures can be readily grown lattice matched to InP with CBOs as large as 1.12 eV (Ref. 91). Apart from having a large CBO, the device operation is not affected by intervalley electron scattering because there are no low lying X or L valleys (see Fig. 6.2). Therefore, this material system holds promise for producing high performing devices with emission in the 3 to 5 μm range.

In Chapter 7, EL results for this II-VI material system was presented. This was the first observation of QC EL in this II-VI material system. Further more, the observation of

EL is a strong indicator that this material system can be used to fabricate QC lasers. The first generation QC structure consisted of 10 repeats of the active/injector period and no cladding layers were used. As a consequence, the FWHM of the emitted light was quite broad (~ 52 meV) and hence gave cause for concern. Generally a broad EL emission could be due to poor well/barrier interfaces or the result of cavity losses.^{10, 11} However, based on the presence of sharp photoluminescence, with no discernible deep levels in the spectra, and x-ray diffraction data that exhibits multiple satellite peaks for that EL sample, it is not suspected that the broadening is due to poor interface quality. Other possible factors include non optimal device design. In an effort to obtain better EL emission properties, several new samples were grown, this time with 30 repeats of the active/injector region. Also, cladding layers were added to minimize light interaction with the heavily doped contact layers and enable light confinement within the core of the QC structure. The LO phonon energy in the II-VI material system is ~ 32 meV. In our early work 2-well active region regions were employed for light generation. With 2-wells active region it is difficult to grow samples with the stringent control necessary to ensure LO phonon resonance between the two lower energy states in the active region. Therefore the 3-well active regions were explored since this design increased the probability of resonant electron depopulation of the lower lasing state. This is critically important for the reduction in the threshold condition for QC lasing. As done in Chapter 6 and 7, the 3-well active region was modeled using simulation software and the grown samples were thoroughly investigated using FTIR absorption spectroscopy.

In the III-V material system the material parameters that are used for simulations are well established as a result of several decades of intense research. In the case of the

II-VI system this is not the case. In this chapter test a samples was grown to verify the accuracy of the simulation parameters in predicting the energy level distribution with the core of the QC laser. To this end, a 2-well ACQW test sample was designed for ISB absorption at 3.3 μm and subjected to FTIR absorption spectroscopy so that a comparison could be made between the results for the simulation and the grown structure.

The gain of the QC laser as described in (2.13) is inversely proportional to the emission linewidth(γ_{23}) of the device.

$$G_{QCL} = \left(\frac{4\pi q^2}{\epsilon_0 n \lambda} \frac{z_{23}^2}{2\gamma_{23} L_p} \right) \times \left(\frac{\eta_i J}{q} (\tau_3 - \tau_2) \right) N \Gamma \quad (2.13)$$

Generally, the linewidth of semiconductor lasers is a testament to the quality of the well/barrier interfaces. In order to observe the quality of the interface, a cross section of grown ACQW samples was prepared for analysis with SEM and TEM.

8.2 Experiment

As stated earlier, the 2-well active regions design of our earlier QC structures made it difficult to grow samples with **e1-e2** separation that is exactly resonant with the LO phonon energy (~ 32 meV) of the II-VI material. Therefore, in this study the QC structure design was modified to contain 3-well active regions to ensure better control of the lower lasing energy state separations. EL structures were designed for emission nominally at 3.35 and 4.87 μm to demonstrate coverage of the 3 – 5 μm range. Calibration samples were grown to establish the desired alloy compositions, doping levels and the CBO of the heterostructures. Further details on growth and calibration can be found in Chapter 7.

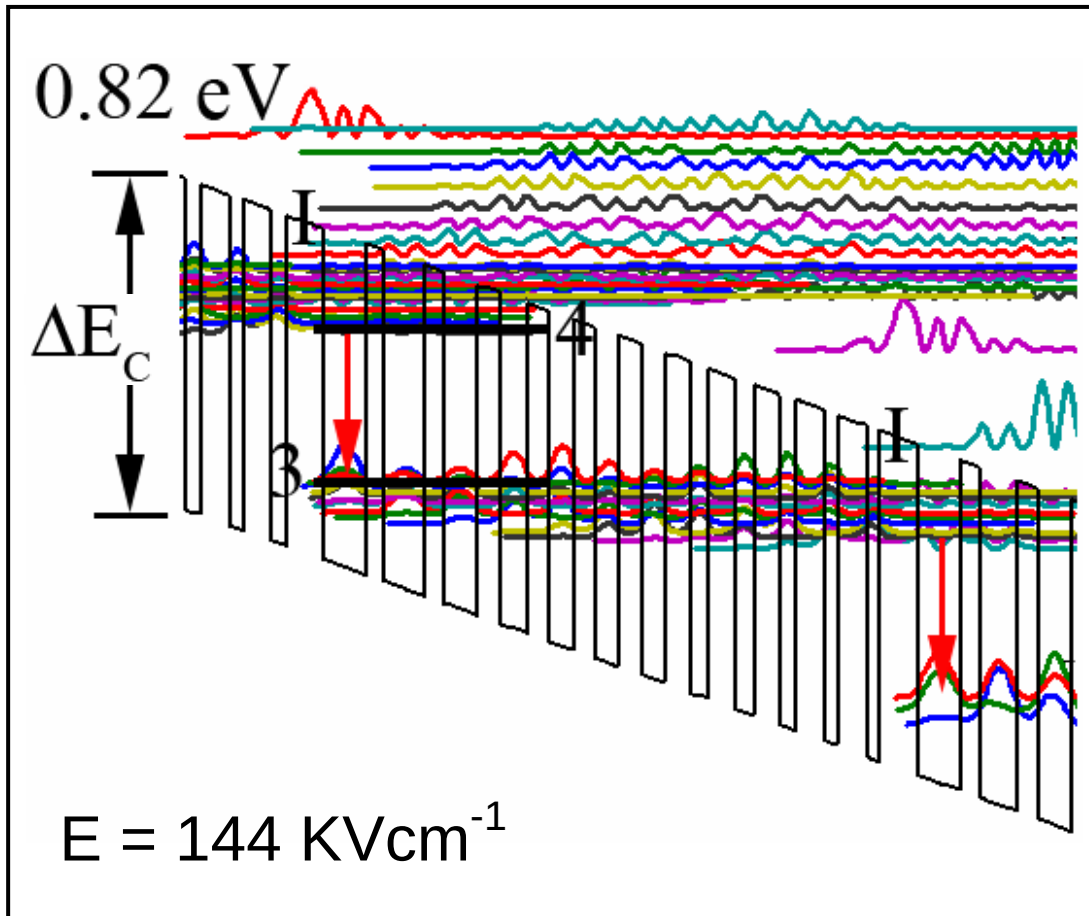


Figure 8.1: Simulation results showing the modulus square of the wave functions in one period of a 3-well EL structure that was design to emit at $3.35 \mu\text{m}$.

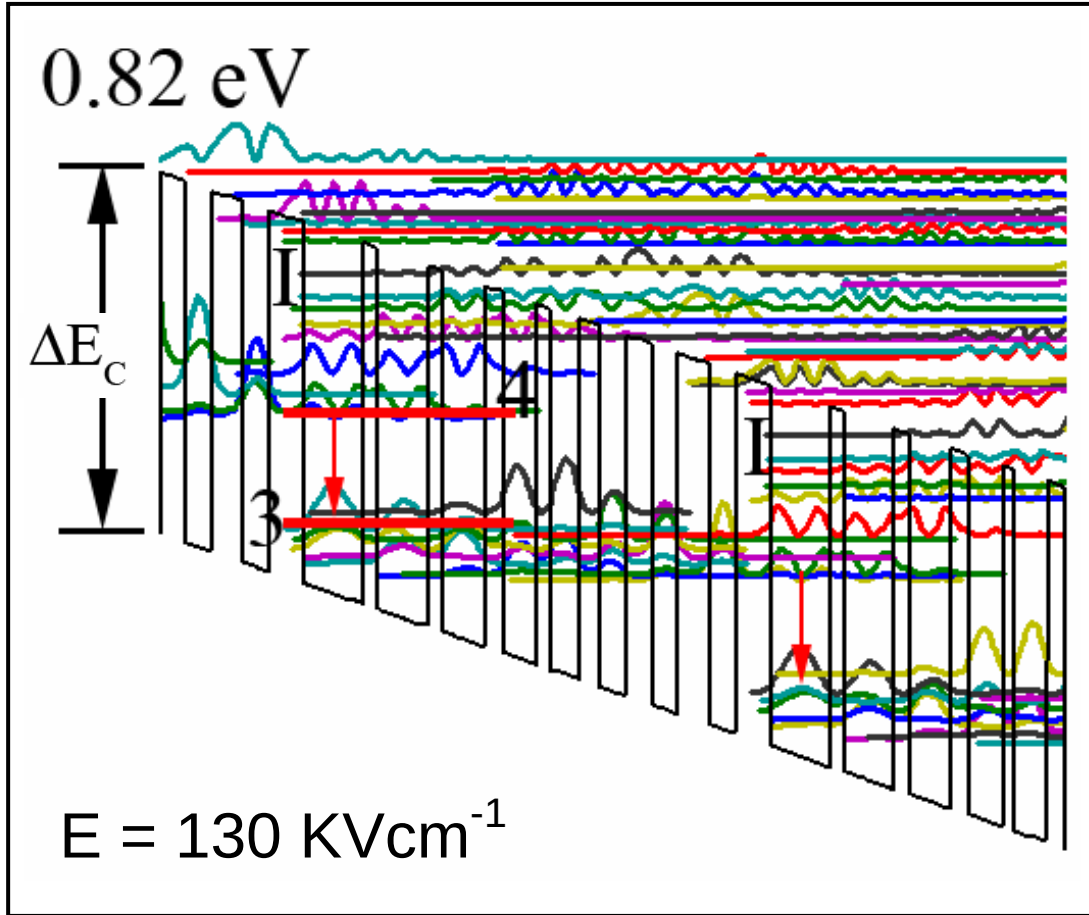


Figure 8.2: Simulation results showing the modulus square of the wave functions in one period of a 3-well EL structure that was design to emit at 4.87 μm .

The CBO for $\text{Zn}_{0.48}\text{Cd}_{0.52}\text{Se}/\text{Zn}_{0.24}\text{Cd}_{0.18}\text{Mg}_{0.58}\text{Se}$ used in this work was 0.82 eV while the effective mass for the well barrier material was 0.1892 and 0.1292, respectively.²⁸ The layer sequences for one period of the 3.35 and 4.87 μm EL structures starting from the injection barrier are as follows:

22/26/11/23/12/20/13/17/12/15/13/14/14/13/15/11/16/10/16/9/17/8/17/8 and

20/35/7/30/8/25/10/20/7/18/11/16/15/15/18/15, respectively. The layer thicknesses are given in angstroms and the barrier layers are in bold. The Cl-doped layers are underlined and the active regions are in italics.

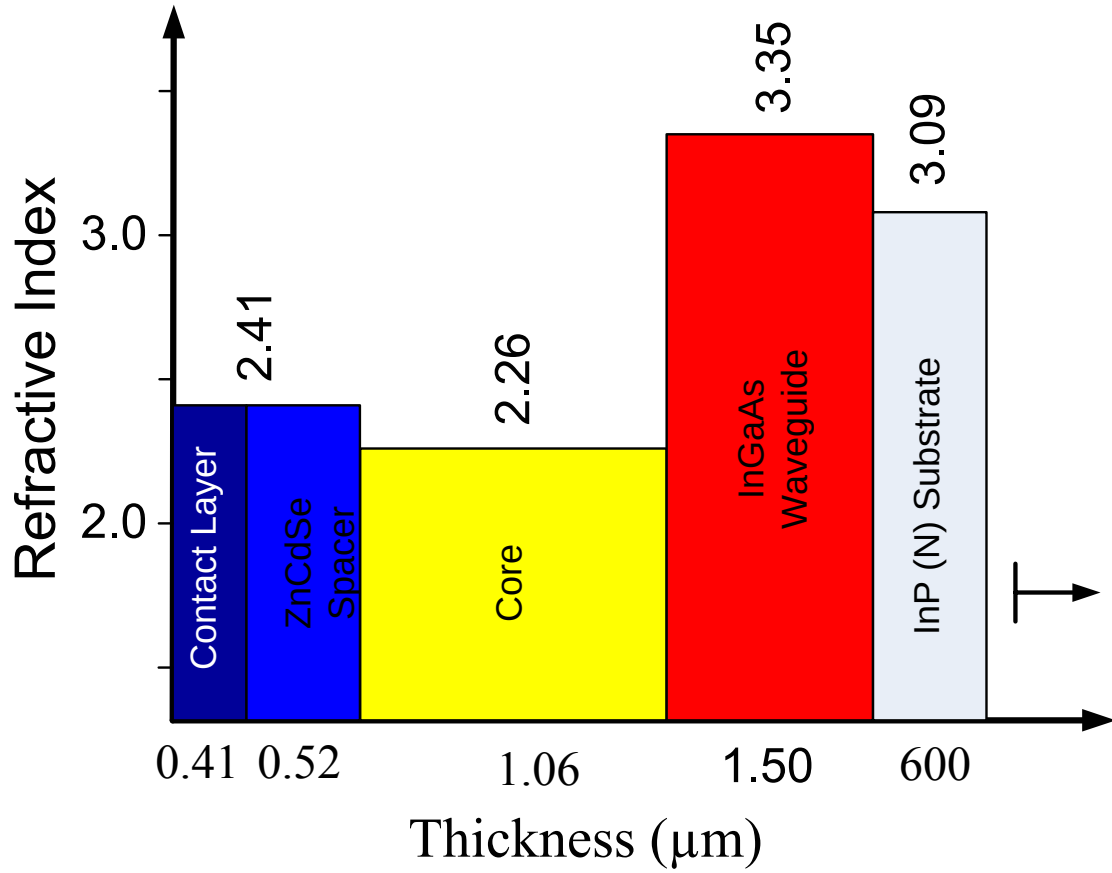


Figure 8.3: Index profile for EL sample A2710. A thick InGaAs layer was grown to prevent light from leaking out through the substrate.

Two waveguide designs were explored. In the first design, a 1.5 μm InGaAs:Si ($n \sim 1 \times 10^{17} \text{ cm}^{-3}$) layer was grown on the substrate side of the core (see Fig. 8.3). In this design, most of the emitted light would be confined in the InGaAs layer. This structure was designed so that part of the confined mode would overlap with the core so that there is optical gain.

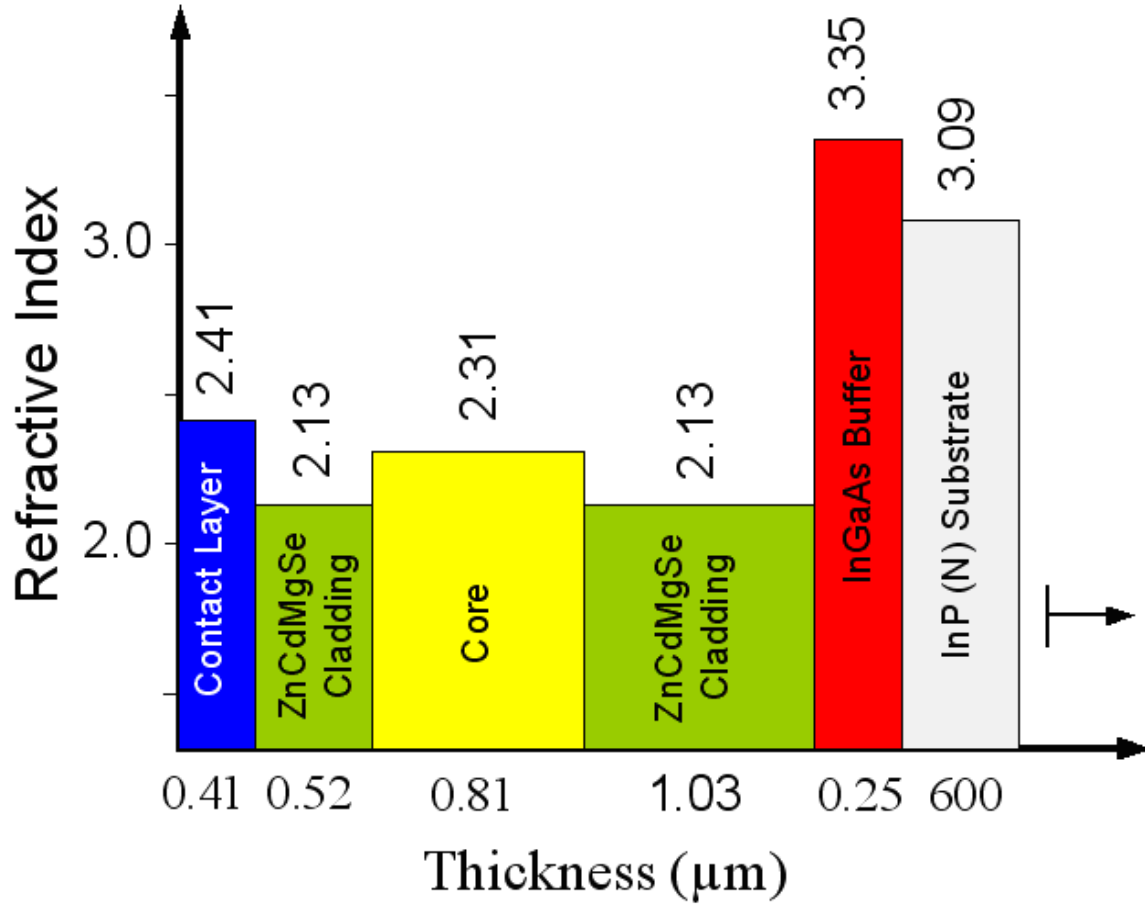


Figure 8.4: Index profile for EL sample A2738. This structure was designed to confine light using quaternary cladding layers.

In the second design show in Fig. 8.4, 1.03 and 0.52 μm doped $\text{Zn}_{0.24}\text{Cd}_{0.18}\text{Mg}_{0.58}\text{Se}:\text{Cl}$ ($n \sim 3 \times 10^{17} \text{ cm}^{-3}$) layers were grown at the substrate and top contact side of the EL structure, respectively. The refractive indices for the ternary and quaternary II-VI layers in the mid-IR were calculated using Ref. 97. The refractive index of the core was determined based on the percentage of ternary and quaternary material that in that region. Shorter injectors were also incorporated in the second design to reduce the device resistance and doping requirements of the structure. Furthermore, since the device gain is

inversely proportional to the period length, a reduction in the injector length improves our chances of observing gain in this QC structure. The samples were grown in Riber 2300P dual chamber system as described in Chapter 2. All grown samples were characterized using x-ray diffraction, photoluminescence (PL) and FTIR spectroscopy.

A 2-well ACQW test-sample was grown to assess the accuracy of the simulation results at short wavelengths. Also, this was done to determine possibility of fabricating QC lasers with emission near $3.0\ \mu\text{m}$. The test sample had thick quaternary barrier layers separating 2-well active regions, rather than the more complex injector structure grown for the EL structures. The layer sequence for one period of the test sample designed for absorption at $3.06\ \mu\text{m}$ is as follows: **110/23/12/20**, where layer thickness is given in angstroms, the barrier layers are indicated in bold and the doped wells are underlined. A simulation based on the Schrödinger equation and the transfer matrix technique was used to predict the energy level distribution in this test-sample. The asymmetric coupled quantum wells of the test-sample were repeated 30 times and the wells were doped ($n_{Cl} \sim 5 \times 10^{18}\ \text{cm}^{-3}$) to enable FTIR absorption measurements.

8.3 Results and Discussion

The two EL samples with optimized QC designs (A2710 and A2738) were investigated using PL and FTIR. In order to observe the PL emission from the core region of the EL structure, the thick contact layer was etched off using a dilute solution of bromine/methanol. The PL measurements were done on the EL samples A2710 and A2738 using the 325 nm line of a He-Cd laser. The PL results obtained are shown in Fig. 8.5. The absence of deep level emission indicates that the material is of high quality.

Also, the FWHM of 36 and 33 meV that were obtained for these samples suggest that the well/barrier interfaces for these II-VI structures are of good quality.

The FTIR absorption spectrum for sample A2710 is shown in Fig. 8.6. Absorption peaks corresponding to **e1-e4** and **e3-e4** transitions were observed at 0.415 eV (2.99 μ m) and 0.329 eV (3.78 μ m), respectively, suggesting QC emission at about 3.8 μ m is possible.

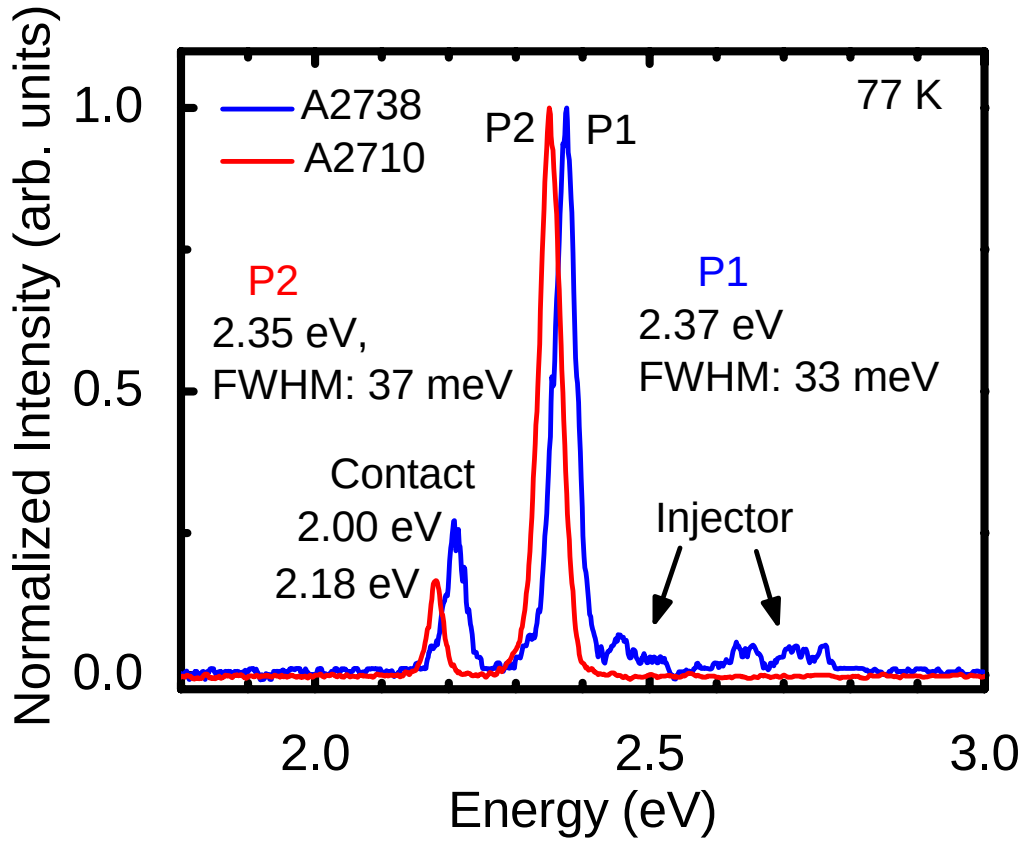


Figure 8.5: Photoluminescence spectrum for QC structures A2710 and A2738 at 77 K. The dominant emission peaks from the active region were clearly visible when the samples were etched with a bromine/methanol solution. Lower intensity emissions can be

seen for the contact layer at 2.18 and 2.20 eV, respectively. Emission could also be detected for the injector layers of sample A2738.

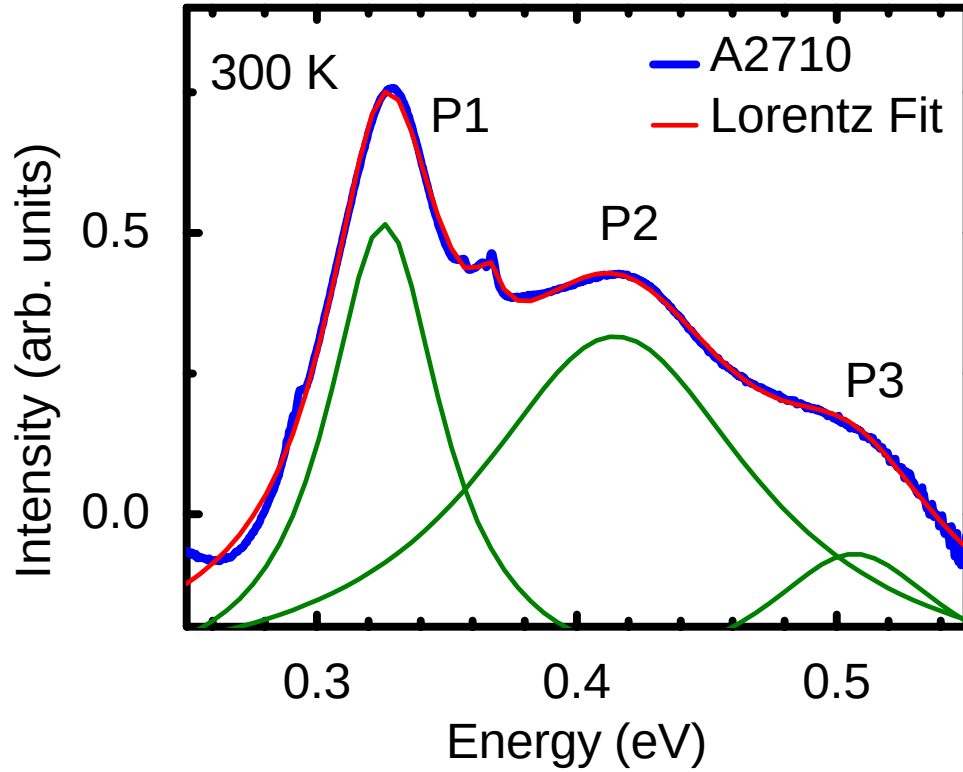


Figure 8.6: FTIR absorption spectrum for the unbiased sample A2710 at 300 K. A Lorentz fit was performed to identify the absorption peak. The absorption energy corresponding to the identified peaks can be seen in Table 8.1.

The EL samples were processed into QC emitter structures as described in Chapter 7. I-V measurements results for the emitter structures are shown as insets in Figs. 8.7 and 8.8.

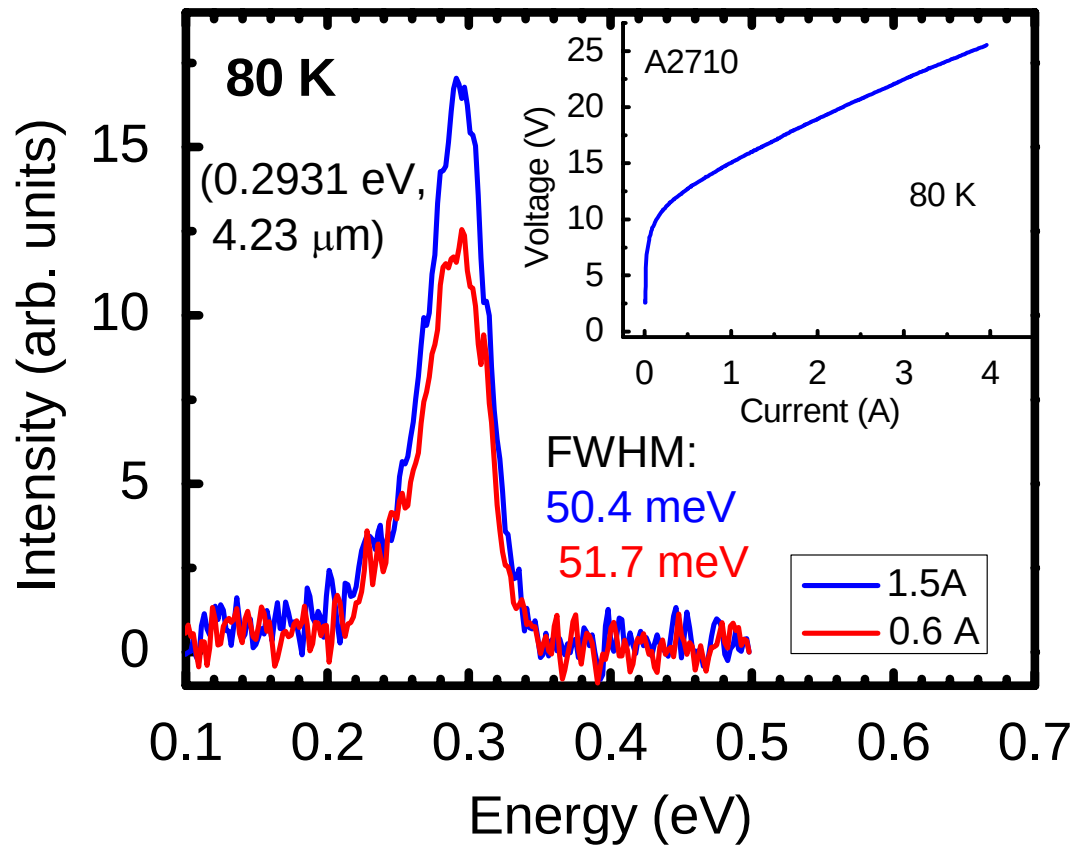


Figure 8.7: Electroluminescence emission for sample A2710 at 80 K. Emission with a FWHM of 51 meV was observed at 0.2936 eV (4.23 μm) when a bias of 144 KV/cm was applied. The I-V curve for the device can be seen in the inset. The turn on voltages for the device was ~ 10 V at 80 K.

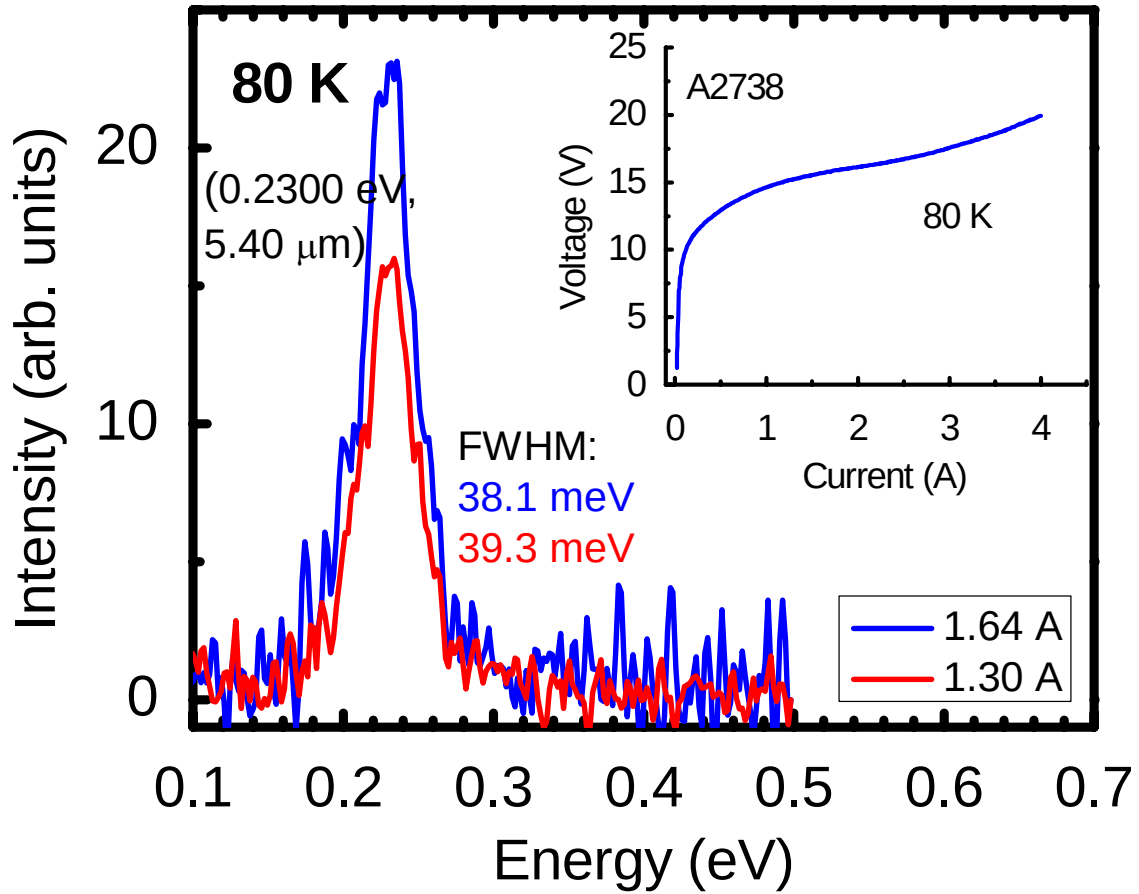


Figure 8.8: Electroluminescence emission for sample A2738 at 80 K. Emission corresponding with a FWHM of 33 meV was observed at 0.2300 eV (5.40 μm) when a bias of 130 KV/cm was applied. The I-V curve for the device can be seen in the inset.

The turn on voltages for the device was $\sim 11\text{V}$ at 80 K.

These I-V measurements made at 80 K indicate normal QC behavior. Using the FTIR in the step scan mode, the QC samples were also investigated for emission at 80 K.

Electroluminescence was observed for samples A2710 and A2738 at 4.23 and 5.4 μm , respectively (see Figs. 8.7 and 8.8). The results from these two samples are summarized in Table 8.1.

Sample	Energy transitions	Predicted (eV) Unbiased	Measured (FTIR) (eV) Unbiased	Measured (EL) (eV) Biased
A2710	P1 (e3 – e4)	0.3535 (3.51 μm)	0.329 (3.78 μm)	0.293 (4.23 μm)
	P2 (e1 – e4)	0.4298	0.04149	-
	P3 (e1 – e5)	0.5192	0.5068	-
A2738	e3 – e4	0.225 (5.52 μm)	-	0.230 (5.40 μm)

Table 8.1: Summary of simulation results and the measured FTIR absorption data for samples A2710 and A2738 at zero bias (300 K). The EL results were obtained for samples biased at 80 K.

The EL emission for sample A2710 has a FWHM of 51 meV, while sample A2738 has a FWHM of 38.8 meV. Since EL linewidth is related to the emission energy, a more accurate indication of quality is obtained from the ratio of $\Delta E/E$, where ΔE is the linewidth of the peak and E is the peak energy. The ratio $\Delta E/E$ was calculated for the EL spectra of Figs. 8.7 and 8.8, and values of 0.174 and 0.168 we obtained for samples A2710 and A2738, respectively. These numbers constitute a slight improvement over the $\Delta E/E$ of 0.201 calculated for our previously reported EL structure, which did not contain any cladding or waveguide layers.⁸ We tentatively attribute this slight improvement in

$\Delta E/E$ to the presence of an InGaAs waveguide layer in A2710 and ZnCdMgSe quaternary cladding layers in A2738. We believe that improvements in the waveguide and device structure design, as well as optimization of the doping levels in the core, will produce further improvements in the device properties.

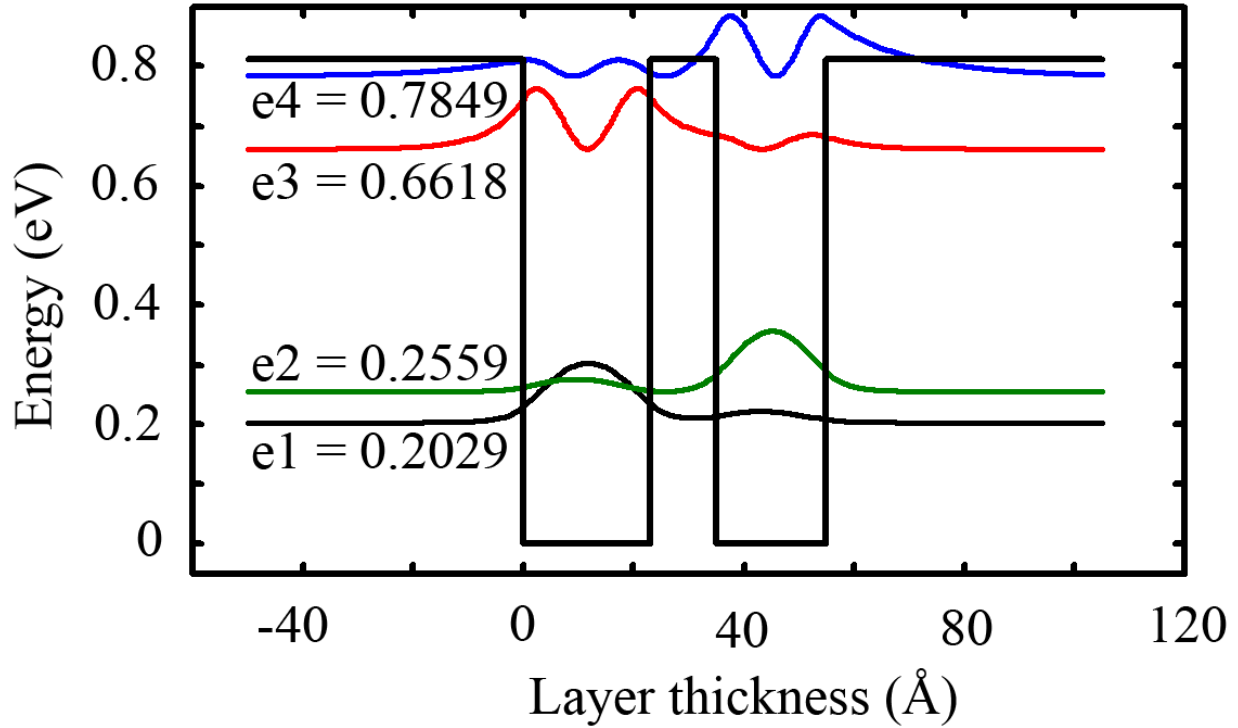


Figure 8.9: Simulation results showing the modulus square of the wave function for the test sample A2732. The simulation results for the unbiased test sample at 300 K (110/23/12/20) predict **e1-e3** and **e2-e3** intersubband transitions at 0.449 and 0.406 eV, respectively.

The simulation results for the 2-well ACQW test sample that was study in this work is shown in Fig. 8. 9. The grown sample (A2732) was subjected to PL analysis to assess the material quality. Excitation was performed with the 325nm line of a HeCd laser. The

absence of deep level emission in the PL spectrum shown in Fig. 8.10, indicates that the material quality is good. This sample was processed into a multiple pass waveguide structure with 45° facets for FTIR absorption spectroscopy measurements, which were performed at room temperature. A Lorentz fit was performed to identify the absorption peaks (see. Fig. 8.10).

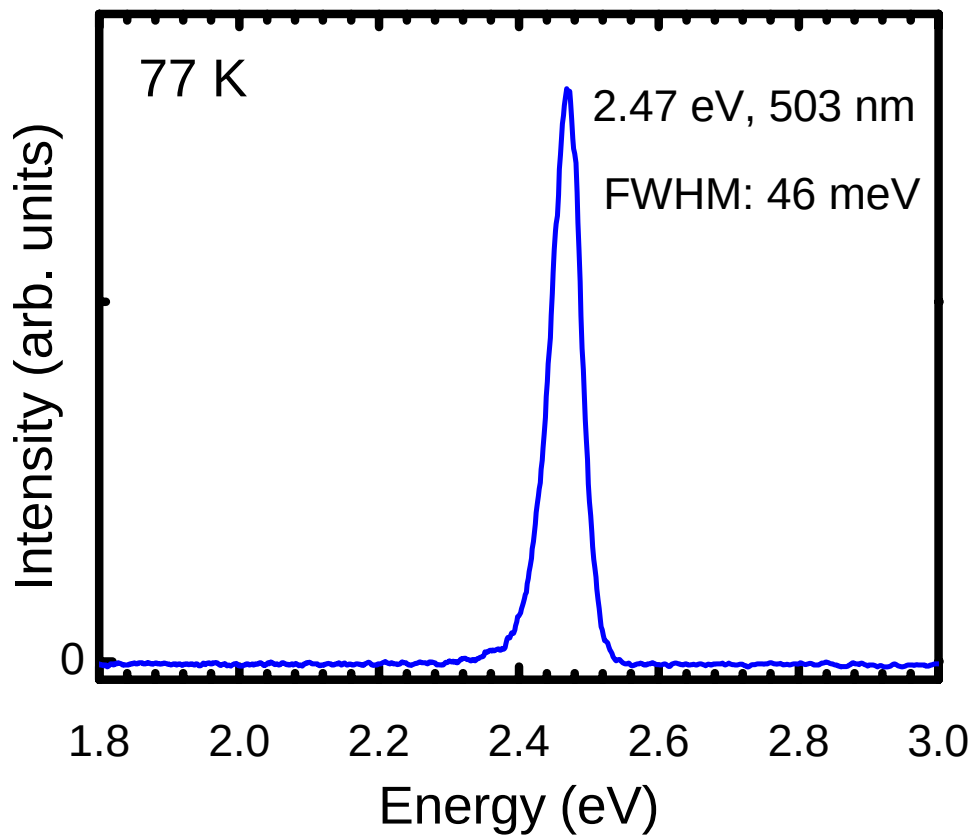


Figure 8.10: PL spectrum for ACQW test sample A2732. The absence of deep level emission indicates a low defect density.

The results, displayed in Fig. 8.11 and Table 8.2, show a slight deviation between the predicted and measured values. This may be due to monolayer scale fluctuations in the barrier width and/or to the fact that the simulation parameters for this material system are not fully optimized.^{12, 13} The measured e2 – e3 transition energy of 0.3507 eV suggests that with only minor adjustments to the growth parameters, a QC structure could be made to emit at $\sim 3.5 \mu\text{m}$ using this material composition.

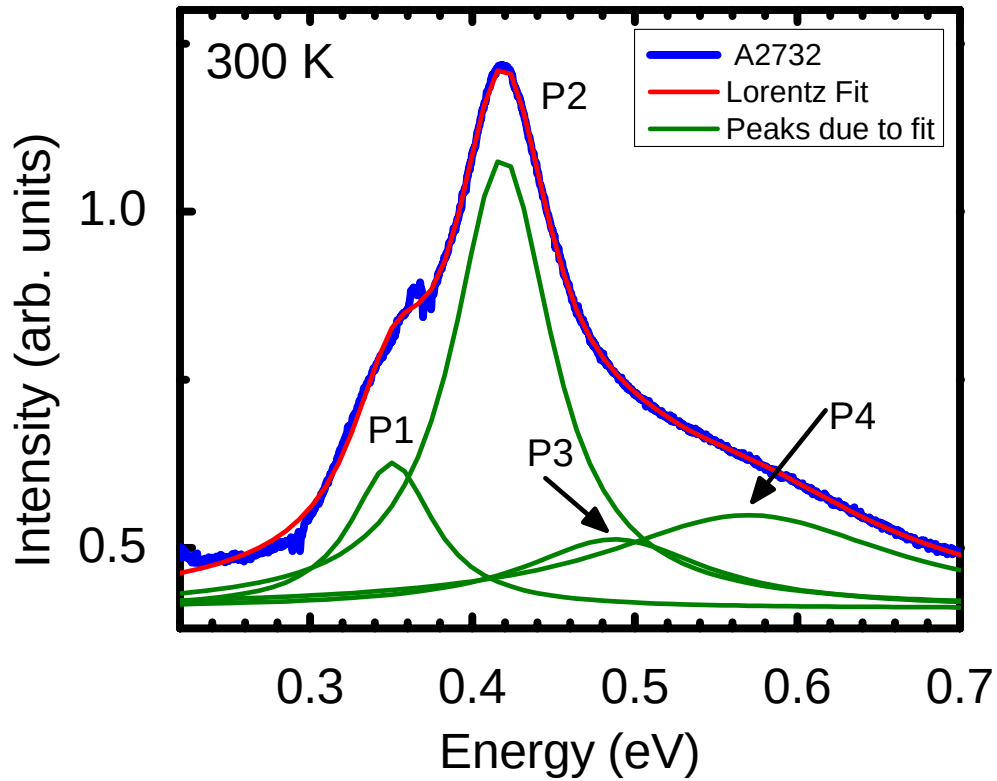


Figure 8.11: FTIR absorption spectrum for test sample A2732 at 300 K. A Lorentz fit was performed to identify the absorption peaks. The absorption energy corresponding to the identified peaks can be seen in Table 8.2.

Energy transitions	Predicted (eV)	Measured (eV)
P1 (e2 – e3)	0.4062 (3.06 μ m)	0.3507 (3.54 μ m)
P2 (e1 – e3)	0.4589	0.4182
P3 (e2 – e4)	0.5293	0.4877
P4 (e1 – e4)	0.5820	0.5697

Table 8.2: Comparison between absorption peaks predicted by simulation and measured by FTIR for the unbiased test sample (A2732) at 300 K.

In an effort assess the quality of the II-VI wells and barriers interface, a ACQW test samples (**110/34/6/30/110**, barrier layers are in bold) was grown and subsequently processed for analysis with SEM and TEM.⁹⁸ The SEM image for the cleaved test sample can be seen in Fig. 8.12. On close examination of the SEM image, the thin central barrier of the ACQW structure can be identified (see the area between the arrows in Fig. 8.12). In an effort to get a clearer image of the interface, the sample was thinned and analyzed using TEM. From the SEM image in Fig. 8.13, the very thin central barrier (6 μ m nominal thickness) can clearly be seen. The atomic arrangement in the vicinity of this central barrier seems to be consistent with what is expected from a defect free crystalline lattice. These images indicate that II-VI MQW structures with high quality interfaces can be grown.

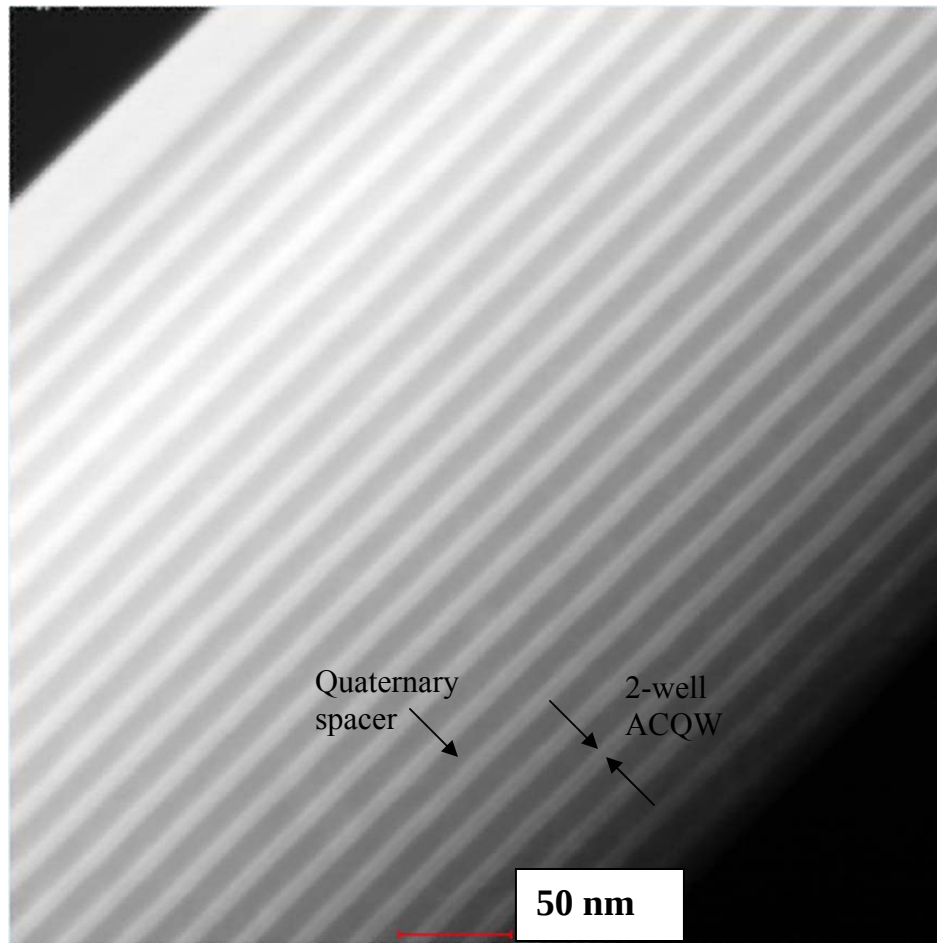


Figure 8.12: SEM image of a cleaved 2-well ACQW test sample.

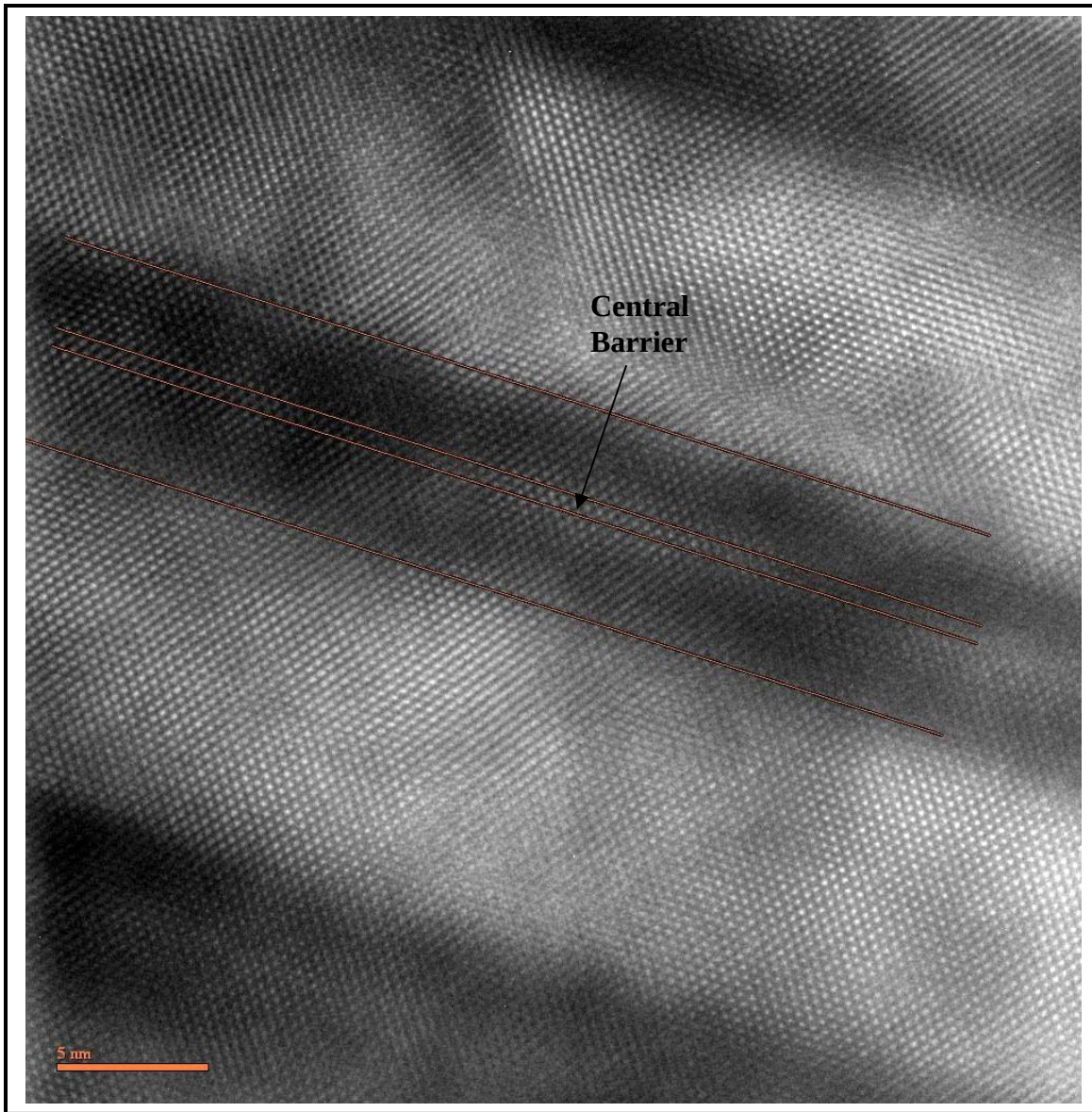


Figure 8.13: TEM image of the 2-well ACQW sample with a central barrier that is ~ 6 Å thick.

8.4 Summary/Conclusion

Two QC EL structures were designed for emission within the first atmospheric window. These structures were grown and investigated for QC electroluminescence. Emission was observed at 4.23 and 5.40 μm . Quaternary cladding layers were added between the core and the contact layers for the purpose of light confinement in sample A2738, while an InGaAs waveguide layer was used in A2710. A slight reduction in the value of $\Delta E/E$ was obtained for these new structures, compared to our previously reported EL results. We conclude that improvement in the waveguide and device structure design, as well as optimization of the doping levels in the core, will result in improved EL characteristics.

A test sample consisting of QC active regions separated by thick quaternary barrier layers was grown to investigate the possibility of producing QC structures that emit at the short wavelength end of the first atmospheric window (3 – 5 μm). The simulation results for the test sample predicted that the **e2 – e3** electronic transition would be at 0.4062 eV (3.06 μm) while FTIR absorption for that sample was observed at 0.3507 eV (3.54 μm). The small discrepancy between the simulation and FTIR data, suggests that the II-VI material simulation parameters may need to be optimized. Nevertheless, these results confirm that QC structures with emission wavelengths between 3.0 – 4.0 μm can be produced using this II-VI material system.

The cross-section of a II-VI ACQW test sample was viewed with SEM and TEM in order to make an asses the well/barrier interface quality. The very thin central barrier layer in this test sample could be seen using SEM. Further analysis of the sample using TEM showed an arrangement of atoms in the vicinity of the well barrier boundary that is

consistent with high quality crystalline material. This SEM result confirms that II-VI MQW structures can be grown with excellent interfaces.

Chapter 9

Summary and Future Directions

9.1 Summary of Current Work

The QC laser is a very complex MQW device with a core that when biased, is responsible for generating light at a predetermined wavelength. The emission energy or wavelength can be tuned by adjusting the thicknesses of the active region's wells and barriers. The core of the QC laser is also critically important in establishing the conditions for population inversion or lasing. To achieve lasing, injector and collector regions of the core must be designed to maximize electron transport to and from the active regions. Additionally, the active region should be designed so that there is rapid electron depopulation of the lower lasing state due to LO phonon resonance. In an effort to move closer to the goal of realizing the first II-VI QC laser, the following work was done.

A QC EL structure was designed for emission at 4.5 μm using material parameters such as electron effective masses and a conduction band offset that was established in previous work done by our group and presented in Chapter 4. The first QC EL structure was designed with very simple 2-well asymmetric coupled quantum well (ACQW) active regions. Given that extensive work was not done to establish the material parameters of this material system, test samples were designed and grown to verify the accuracy of the material parameters. The test samples were a modification of the QC structures where the injector regions were replaced with thick barrier layers. The QC structures were designed using a software package that is based on the Schrödinger's equation and the transfer

matrix technique. A Matlab-based program was written to model the energy level distribution of the ACQW test structures. Then, test samples were grown using MBE and subjected to FTIR absorption spectroscopy to determine the energy level distribution in the active region. Comparisons were made between the simulation and FTIR results for the test samples to determine if growth or material parameters optimizations were necessary before undertaking the long and complex growth of QC structures.

EL QC structures designed for emission in the 3 – 5 μm atmospheric window were grown using MBE. These samples were analyzed using FTIR absorption spectroscopy in order to determine the energy level distribution in the active region. These measurement results for the unbiased QC structure were compared with those obtained for test samples with similar active regions. These comparisons revealed that a simple ACQW test sample can be used to predict the optical properties of the QC device before undertaking the long and complex growth. Furthermore, EL structures were grown and processed into QC emitters using photolithography and electron beam contact deposition. QC emission was observed within the 3 – 5 μm range, in very good agreement with the design. This is the first observation of II – VI QC emission. These results therefore confirm that the II-VI material system is a viable option for producing QC lasers.

With the laser core successfully designed and functional, the next issue that had to be resolved was light confinement within the laser core (or gain material). In order to ensure light confinement, the laser core must be surrounded with a material whose refractive index is smaller than the average of the core. With this in mind, two light confinement approaches were explored. First a QC laser was designed for emission at 4.9 μm with a core that was surrounded by $\text{Zn}_{0.24}\text{Cd}_{0.18}\text{Mg}_{0.58}\text{Se}$ a cladding. In the second

approach, a thick InGaAs guiding layer was inserted between the QC laser core and the InP substrate. This InGaAs layer thickness was chosen so that part of the guided mode would reside in the core to ensure optical gain.

Steps were taken to improve the optical gain of the II-VI QC laser. Given that the gain is inversely related to the electron lifetime in the lower lasing state, a 3-well active region design was used to ensure that the lower lasing states energy separations are resonant with the LO phonon energy of the material. The optical gain is also inversely proportion to the length of the injector/active region period (see equations 2.13). Therefore, the optimized QC lasers were designed with shorter injector region. These optimized structures were characterized with PL, HRXRD and FTIR before being processed into QC emitters. The EL result at 80 K showed an improvement in the output light intensity and a reduction in $\Delta E/E$ when compared to the first generation EL sample which had no cladding layers. These improvements can be attributed to improved optical confinement and emission efficiency.

Generally, the simulation and measured results for the QC structure showed very good agreement for devices designed to operate at the lower energy end of the first atmospheric window. At the higher energy end, there seemed to be some deviation. OC lasers that are designed to operate at short wavelengths using wide bandgap materials require barriers that could be as thin as two monolayers. Therefore, this disagreement may be due to the increased sensitivity of the emitted light to monolayer scale error in the barrier thicknesses. This deviation could also be due to an increased sensitivity to errors in the material parameters for devices that are designed to operate at higher energies.

Finally, the QC structures were characterized with PL and HRXRD to evaluate the material and interface quality. Also, as test sample was imaged with high resolution SEM and TEM. Overall, the results that were obtained strongly suggest that QC devices can be grown with material and interface quality that are as good as III-V materials.

9.2 Future Directions

The material quality and optical properties of the QC structures grown thus far strongly suggest that the II – VI material system has great potential for producing IR lasers in the first atmospheric window. The demonstration of electroluminescence is a very significant step since this proved that light generation in a II – VI laser core is possible. In order realize an efficient QC laser the following may be explored.

9.2.1 Establish Material Parameters

Throughout this research effort, QC structures were modeled for operation at the extreme end of the first IR window (3 – 5 μm). Most of the devices studied were designed to operate at the long wavelength end where the simulation results tend to agree very well with the FTIR and EL results. The few devices that were designed for short wavelength operation showed significant deviation from the measured results. This discrepancy could be due to the sensitivity to monlayer scale fluctuation in the barrier layer thickness within the active region. This disagreement could also be due to inaccuracies in the simulation parameters such as the effective masses and CBO used for the device modeling. MQW samples should be grown to determine the source of the problem. In the event that the discrepancy is not due to barrier thickness error, CER

studies should be done to establish to the CBO for these very narrow quantum wells structures since the energy level distribution has greater sensitivity to CBO than slight errors in the effective masses.

9.2.2 Growth of InGaAs Contact on ZnCdSe

The performance of QC lasers degrade due to thermal heating, therefore everything must be done to reduce the overall resistance of the device. One area of concern with the II – VI devices is the quality of the metal contacts. In some instances the metal adhesion to the ZnCdSe contact layer was a major issue since the metal would detach. Also there were times when the measured turn-on voltage was higher than expected due to high contact resistance. These problems may be due to the incompatibility of III-V process with the II – VI contact layer material. In the past our group was able to successfully grow ZnSe on GaAs. Using the expertise gained in that research endeavour, InGaAs growth on ZnCdSe should be explored since this would enable compatibility with well established III – V processing technology.

9.2.3 $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$ Cladding for Light Confinement

The gain of the QC laser is directly proportional to the light confinement factor Γ , therefore steps must be taken to keep Γ at a maximum. Further detail on this issue can be found in section 2.3.2.3 of this thesis. In this work I have resorted to using ZnCdMgSe cladding layers with a bandgap of ~ 3.1 eV (77 K) because it can be grown lattice matched to the InP substrate. A QC structure was grown with a 0.52 and 1.03 μm thick $\text{Zn}_{0.24}\text{Cd}_{0.18}\text{Mg}_{0.58}\text{Se}$ cladding layers (Fig. 8.4). A high defect density was observed in the

top cladding layer when that sample was view with the Normarski optical microscope. This defect density was not observed for bulk quaternary materials grown directly on InP substrates. The degradation in cladding layer material quality is of concern because this could lead to a reduction in the lifetime of the fabricated QC device. Degradation in bulk quaternary materials directly grown in InP is usually observer when the bandgap exceed 3.2 eV. Soheli et al (Ref. 29) was able to demonstrate that high quality $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$ can be grown with bandgaps varying from 3.59 to 3.66 eV at 77 K. This report²⁹ suggest that the ternary material can be grown with refractive indices that are less than that of the quaternary. Therefore, $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$ should be explored for confining light in II – VI QC lasers.

9.2.4 Strain Compensated QC Structures

The CBO of the lattice matched $\text{Zn}_{0.48}\text{Cd}_{0.52}\text{Se}/\text{Zn}_{0.24}\text{Cd}_{0.18}\text{Mg}_{0.58}\text{Se}$ used in this research was enough to enable the fabrication of devices that could operate at $\lambda \sim 3.5\mu$. To operate at shorter wavelengths, strain compensation could be used to bring about an increase in the CBO. Alternatively, a strain balance structure could be grown where the quaternary barrier is replaced by the ternary $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$. This second approach is very attractive for the following reasons:

- 1) The material quality of the quaternary tends to degrade when the bandgap exceeds 3.2 eV while $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$ can be grown with a bandgap as large as 3.66 eV without material quality deterioration.
- 2) In our MBE system only one Cd cell is available in the II – VI chamber therefore, the growth rate of the well and barrier material cannot be changed

independently. The growth rate of the quaternary material used in this research is approximately three times that of the ternary well material. With growth rates of 0.3 and 0.9 $\mu\text{m/h}$ for the well and barrier layers, respectively, growth of a QC laser with 40 repeats would require in excess of 10 hours. The use of the $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$ barrier would mean that the growth rate of the well material could be increased to values similar to that of the barrier material. Moreover, this change would result in a reduction in the growth time of the QC laser.

- 3) The gain of the QC laser is inversely proportional to the effective mass of the materials used. Therefore, the switch from the quaternary to the ternary would result in a reduction in the effective mass of the barrier material.
- 4) A larger confinement factor is possible with a $\text{Zn}_x\text{Mg}_{(1-x)}\text{Se}$ cladding.

The next step in this research effort is to demonstrate QC lasing in this II – VI material system. The research directions outlined in this section should result in the realization of a II – VI QC laser operating within the first atmospheric window.

Appendix A

1. Growth sheet for the first designed II-VI Electroluminescence structure

4.5 μm II-VI QC Luminescence Structure

design by K.J. Franz -- 70423

Total growth: 0.5182 μm

$$n_s = 7 \times 10^{11} \text{ cm}^{-2}$$

Special instructions: •Grow on a low-doped ($< 2 \times 10^{17} \text{ cm}^{-3}$) n-type InP substrate. •Doping for the top contact should be as high as possible (2×10^{20} probably is not possible).

	material	layer width ($\text{\AA}$)	n-type dopant (cm^{-3})
cap & top electrical contact	CdSe	90	2.0E+20
	ZnCdSe	1600	2.0E+20
	ZnCdSe	400	3.0E+17
transition in	ZnMgCdSe	10	
	ZnCdSe	24	
	ZnMgCdSe	10	
	ZnCdSe	22	
	ZnMgCdSe	12	
	ZnCdSe	20	3.0E+17
	ZnMgCdSe	16	3.0E+17
	ZnCdSe	20	3.0E+17
	ZnMgCdSe	18	3.0E+17
	ZnCdSe	18	3.0E+17
	ZnMgCdSe	18	3.0E+17
	ZnCdSe	18	3.0E+17
	ZnMgCdSe	20	3.0E+17
	ZnCdSe	16	3.0E+17
	ZnMgCdSe	20	3.0E+17
	ZnCdSe	16	3.0E+17
	ZnMgCdSe	20	3.0E+17
	ZnCdSe	14	3.0E+17
	ZnMgCdSe	22	3.0E+17
	ZnCdSe	14	3.0E+17
	ZnMgCdSe	24	
	ZnCdSe	12	
	ZnMgCdSe	26	
	ZnCdSe	12	
active region <i>repeat 15 times</i>	ZnMgCdSe	30	
	ZnCdSe	34	
	ZnMgCdSe	10	
	ZnCdSe	28	

	ZnMgCdSe	20	
	ZnCdSe	24	
	ZnMgCdSe	10	
	ZnCdSe	22	
	ZnMgCdSe	12	
	ZnCdSe	20	3.0E+17
	ZnMgCdSe	16	3.0E+17
	ZnCdSe	20	3.0E+17
	ZnMgCdSe	18	3.0E+17
	ZnCdSe	18	3.0E+17
	ZnMgCdSe	18	3.0E+17
	ZnCdSe	18	3.0E+17
	ZnMgCdSe	20	3.0E+17
	ZnCdSe	16	3.0E+17
	ZnMgCdSe	20	3.0E+17
	ZnCdSe	16	3.0E+17
	ZnMgCdSe	20	3.0E+17
	ZnCdSe	14	3.0E+17
	ZnMgCdSe	22	
	ZnCdSe	14	
	ZnMgCdSe	24	
	ZnCdSe	12	
	ZnMgCdSe	26	
	ZnCdSe	12	
transition out	ZnCdMgSe	30	3.0E+17
	ZnCdSe	34	3.0E+17
	ZnCdMgSe	10	3.0E+17
	ZnCdSe	28	3.0E+17
	ZnCdMgSe	20	3.0E+17
	ZnCdSe	24	3.0E+17
	ZnCdMgSe	10	3.0E+17
	ZnCdSe	22	3.0E+17
	ZnCdMgSe	12	3.0E+17
	ZnCdSe	22	3.0E+17
	ZnCdMgSe	10	3.0E+17
	ZnCdSe	24	3.0E+17
	ZnCdMgSe	10	3.0E+17
	ZnCdSe	26	3.0E+17
	ZnCdMgSe	10	3.0E+17
	ZnCdSe	28	3.0E+17
	ZnCdMgSe	8	3.0E+17
	ZnCdSe	32	3.0E+17
	ZnCdMgSe	8	3.0E+17
	ZnCdSe	36	3.0E+17
	ZnCdMgSe	8	3.0E+17
	ZnCdSe	40	3.0E+17
	ZnCdMgSe	6	3.0E+17
buffer	ZnCdSe	400	3.0E+17

Buffer	InGaAs	1000	5.0E+17
InP Substrate			

Appendix B

This program calculates the wave function and its modulus square for a two-well asymmetric coupled quantum well system.

```
% Effective mass at E = 0
me = 9.10938e-31;
mbx = 0.181;
mwx = 0.128;
mb0 = me*mbx;
mw0 = me*mwx;

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

% SQW or Coupled QW Structure
b1 = -50;
Device.Well_width1 = 34;
Device.Well_width2 = 28;
Device.Central_Barrier = 10;
w1 = Device.Well_width1;
w2 = Device.Well_width2;
b2 = Device.Central_Barrier;
b3 = 50;

% Bandgap of Well and Barrier Materials
EGb = 3.03;
EGw = 2.08;

% Conduction Band Offset
V = 0.82*(EGb-EGw);

Range = 0.01;
% Energy Levels from ACQW_Roots

%Energy_Levels = [0.2029, 0.2559, 0.6618, 0.7842]; %23/12/20 (B=3.07 &
W=2.08)
Energy_Levels = [0.1218, 0.1688, 0.4343, 0.5663]; %34/10/28 (B=3.03 &
W=2.08)
%Energy_Levels = [0.1093, 0.1627, 0.4185, 0.5527,0.8096]; %34/6/30
(B=3.07 & W=2.08)

figure;
for i =1:length(Energy_Levels); % Start of main Loop

    E = Energy_Levels(i);

    %[AB, CD, FG, HI, JK] = Coefficients(mb0, mw0, E, V, EGb, EGw,
Well_width1, Well_width2, Central_Barrier);
    [AB, CD, FG, HI, JK] = Coefficients(mb0, mw0, E, V, EGb, EGw, Device);
```

```

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

% Region (1)
j = 0;
for i=b1:Range:0;
    j = j+1;
    k1 = sqrt(2*mb*q*(V - E))/h_plank;
    y(j) = ((AB(1,1)*exp(k1*i*1e-10)) );
    a(j) = i;
    b(j) = V;
end

% Region (2)
j2 = j;
for i=0:Range:w1;
    j2 = j2+1;
    k = sqrt(2*mw*q*(E))/h_plank;
    y(j2) = ((CD(1,1)*sin(k*i*1e-10)) + (CD(2,1)*cos(k*i*1e-10)));
    a(j2)=i;
    b(j2) = 0;
end

% Region (3)
j3 = j2;
for i=w1:Range:w1+b2;
    j3 = j3+1;
    k1 = sqrt(2*mb*q*(V - E))/h_plank;
    y(j3) = ((FG(1,1)*exp(k1*i*1e-10)) + (FG(2,1)*exp(-k1*i*1e-
10)) );
    a(j3) = i;
    b(j3) = V;
end

% Region (4)
j4 = j3;
for i=w1+b2:Range:w1+b2+w2;
    j4 = j4+1;
    k = sqrt(2*mw*q*(E))/h_plank;
    y(j4) = ((HI(1,1)*sin(k*i*1e-10)) + (HI(2,1)*cos(k*i*1e-10)));
    a(j4) = i;
    b(j4) = 0;
end

% Region (5)
j5 = j4;
for i=w1+b2+w2:Range:w1+b2+w2+b3;

```

```

        j5 = j5+1;
        k1 = sqrt(2*mb*q*(V - E))/h_plank;
        y(j5) = (JK(2,1)*exp(-k1*i*1e-10));
        a(j5) = i;
        b(j5) = V;
    end

temp = max(y.^Power);

x = 1:j5;
plot(a(x), (scale*(y(x).^Power)./temp) +E, a(x), b(x))
drawnow;

xlabel('Layer thickness (z) (Angstrom)')
ylabel('Energy (eV)')
hold on

end % End of Mail Loop
hold off

```

The functions ACQW_Roots and Roots3 calculates the discrete energy level

```

function ACQW_Roots;
Well_width1 = 34;
Well_width2 = 28;
Central_Barrier = 10;
EGb = 3.03;
EGw = 2.08;
mb0 = 0.1892;
mw0 = 0.1292;
CB0 = 0.82*(EGb-EGw);
Range = 10000;
limit = 5e-10;

E = 0: CB0/Range: CB0;

for i=1:Range;
    x = E(i);
    A = Roots3(mb0, mw0,EGb, EGw,x,CB0,Well_width1, Well_width2,
Central_Barrier);
    if abs(A) > limit;
        B(i) = sign(A)*limit;
    else
        B(i) = A;
    end
end

i=1:Range;
plot(E(i), B(i), 'b')
xlabel('Energy (eV)')
grid

```

```

function M = Roots3(mbx, mw, EGb, EGw, Energy, CB0, Well_width1,
Well_width2, Central_Barrier);

w1 = Well_width1*1e-10;
b2 = Central_Barrier*1e-10;
w2 = Well_width2*1e-10;

V = CB0;
a = w1;
b = w1 + b2;
c = b + w2;

me = 9.10938e-31;
mb0 = me*mbx;
mw0 = me*mw;
h_plank = 1.05457e-34;
q = 1.60218e-19;

E = Energy;

if E == 0;
E=1e-10;
end
if E == V
E = V-1e-9;
end

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

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

M1 = [1, 1; k1/mb, -k1/mb];
Minv1 = [0.5, mb/(2*k1); 0.5, -mb/(2*k1)];

M2 = [0, 1; k/mw, 0];
Minv2 = [0, mw/k; 1, 0];

M3 = [sin(k*a), cos(k*a); (k/mw)*cos(k*a), -(k/mw)*sin(k*a)];
Minv3 = [sin(k*a), (mw/k)*cos(k*a); cos(k*a), -(mw/k)*sin(k*a)];

M4 = [exp(k1*a), exp(-k1*a); (k1/mb)*exp(k1*a), -(k1/mb)*exp(-k1*a)];
Minv4 = [0.5*exp(-k1*a), (mb/(2*k1))*exp(-k1*a); 0.5*exp(k1*a), -
(mb/(2*k1))*exp(k1*a)];

```

```

M5 = [exp(k1*b), exp(-k1*b);(k1/mb)*exp(k1*b), -(k1/mb)*exp(-k1*b)];
Minv5 = [0.5*exp(-k1*b), (mb/(2*k1))*exp(-k1*b);0.5*exp(k1*b), -
(mb/(2*k1))*exp(k1*b)];

M6 = [sin(k*b), cos(k*b);(k/mw)*cos(k*b), -(k/mw)*sin(k*b)];
Minv6 = [sin(k*b), (mw/k)*cos(k*b);cos(k*b), -(mw/k)*sin(k*b)];

M7 = [sin(k*c), cos(k*c);(k/mw)*cos(k*c), -(k/mw)*sin(k*c)];
Minv7 = [sin(k*c), (mw/k)*cos(k*c);cos(k*c), -(mw/k)*sin(k*c)];

M8 = [exp(k1*c), exp(-k1*c);(k1/mb)*exp(k1*c), -(k1/mb)*exp(-k1*c)];
Minv8 = [0.5*exp(-k1*c), (mb/(2*k1))*exp(-k1*c);0.5*exp(k1*c), -
(mb/(2*k1))*exp(k1*c)];

AB = Minv1*M2*Minv3*M4*Minv5*M6*Minv7*M8;
M = AB(2,2);

```

This function computes the value of the wave functions coefficients

```

function [AB, CD, FG, HI, JK] = Coefficients(mb0, mw0,Energy, CB0, EGb,
EGw,Device);

V = CB0;

w1 = Device.Well_width1;
b2 = Device.Central_Barrier;
w2 = Device.Well_width2;

a = w1*1e-10;
b = (w1 + b2)*1e-10;
c = (w1 + b2 + w2)*1e-10;

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

E = Energy;

% Effective mass as a function of energy
mw = mw0*(1 + (E)/EGw);
mb = mb0*(1 + (E - V)/EGb);

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

M1 = [1, 1; k1/mb, -k1/mb];
Minv1 = [0.5, mb/(2*k1);0.5, -mb/(2*k1)];

```

```

I1 = Minv1*M1;

M2 = [0, 1;k/mw, 0];
Minv2 = [0, mw/k; 1, 0];
I2 = Minv2*M2;

M3 = [sin(k*a), cos(k*a);(k/mw)*cos(k*a), -(k/mw)*sin(k*a)];
Minv3 = [sin(k*a), (mw/k)*cos(k*a);cos(k*a), -(mw/k)*sin(k*a)];
I3 = Minv3*M3;

M4 = [exp(k1*a), exp(-k1*a);(k1/mb)*exp(k1*a), -(k1/mb)*exp(-k1*a)];
Minv4 = [(1/2)*exp(-k1*a), (mb/(2*k1))*exp(-k1*a);(1/2)*exp(k1*a), -
(mb/(2*k1))*exp(k1*a)];
I4 = Minv4*M4;

M5 = [exp(k1*b), exp(-k1*b);(k1/mb)*exp(k1*b), -(k1/mb)*exp(-k1*b)];
Minv5 = [0.5*exp(-k1*b), (mb/(2*k1))*exp(-k1*b);0.5*exp(k1*b), -
(mb/(2*k1))*exp(k1*b)];
I5 = Minv5*M5;

M6 = [sin(k*b), cos(k*b);(k/mw)*cos(k*b), -(k/mw)*sin(k*b)];
Minv6 = [sin(k*b), (mw/k)*cos(k*b);cos(k*b), -(mw/k)*sin(k*b)];
I6 = Minv6*M6;

M7 = [sin(k*c), cos(k*c);(k/mw)*cos(k*c), -(k/mw)*sin(k*c)];
Minv7 = [sin(k*c), (mw/k)*cos(k*c);cos(k*c), -(mw/k)*sin(k*c)];
I7 = Minv7*M7;

M8 = [exp(k1*c), exp(-k1*c);(k1/mb)*exp(k1*c), -(k1/mb)*exp(-k1*c)];
Minv8 = [(1/2)*exp(-k1*c), (mb/(2*k1))*exp(-k1*c);(1/2)*exp(k1*c), -
(mb/(2*k1))*exp(k1*c)];
I8 = Minv8*M8;

M9 = [0; 1];

AB = Minv1*M2*Minv3*M4*Minv5*M6*Minv7*M8*M9;
CD = Minv2*M1*AB;
FG = Minv4*M3*CD;
HI = Minv6*M5*FG;
JK = Minv8*M7*HI;

```

Example 1

Two-well ACQW **200/34/10/28/200** (barrier layers in bold)

Barrier bandgap = 3.03 eV

Well bandgap = 2.08 eV

Effective mass of electrons in barrier= 0.181

effective mass of electrons in wells = 0.128

$CBO = 0.82 * (\text{Barrier bandgap} - \text{Well bandgap})$

Results

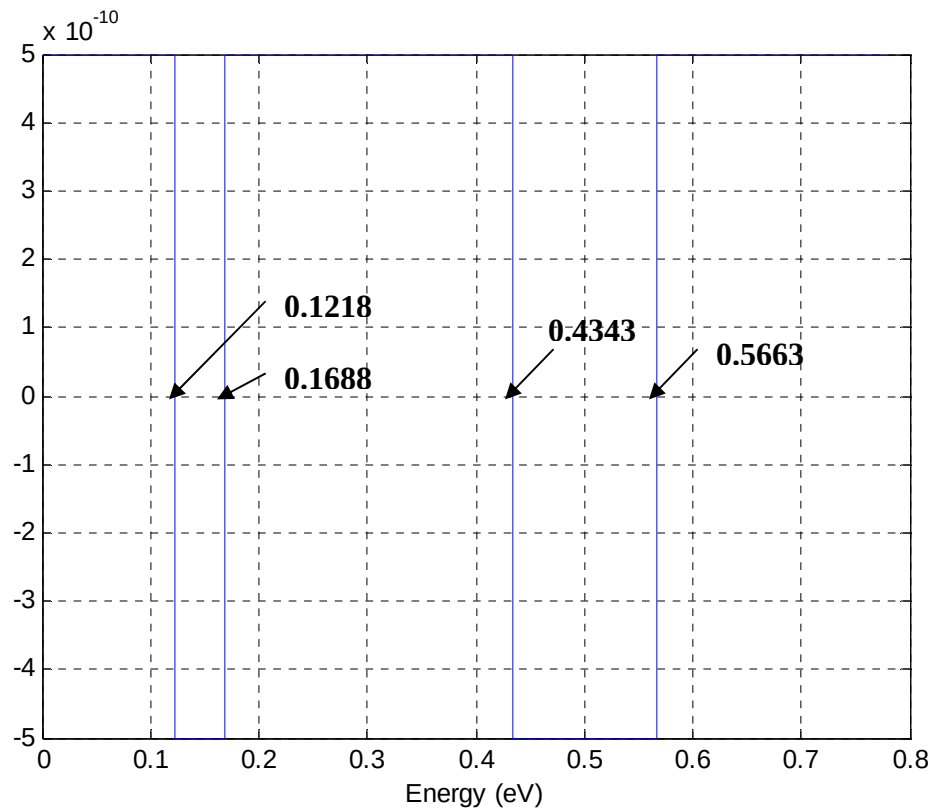


Figure. B.1: Graphical display of the confine energy state for the structure described in example 1. These results were obtained using program *ACQW_Roots*.

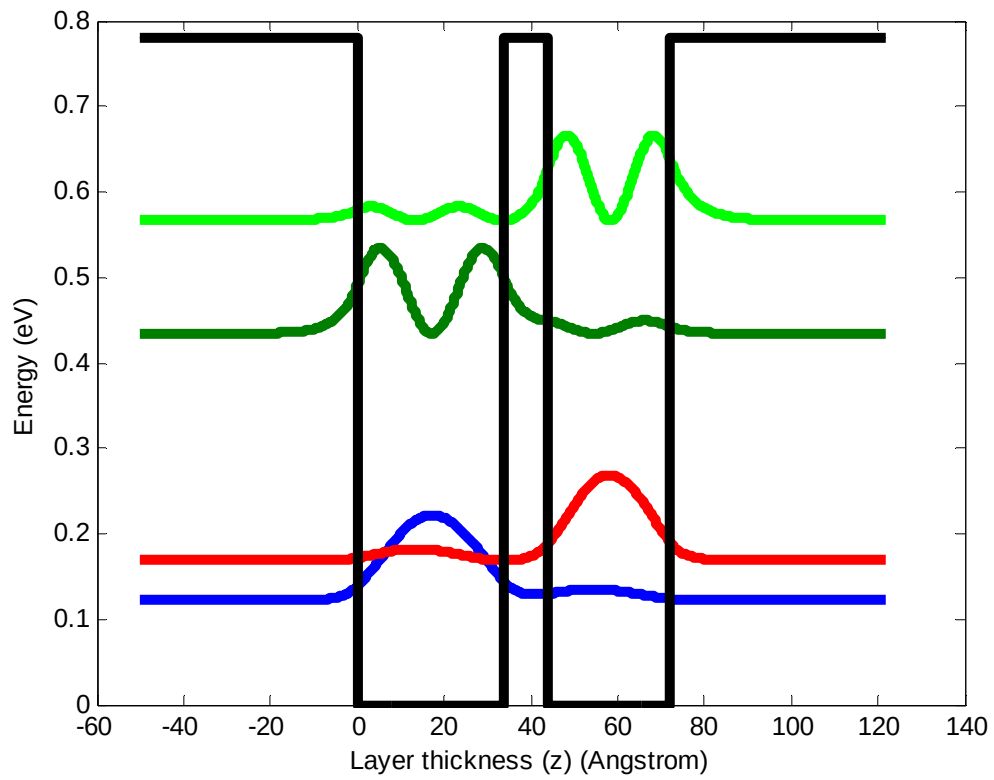


Figure. B. 2: Modulus square of the wave function for the structure described in example 1.

Publications

Journal Papers

- W. O. Charles, Y. Yao, K. J. Franz, Q. Zhang, A. Shen, C. Gmachl and M. C. Tamargo, "Growth of $\text{Zn}_x\text{Cd}_{(1-x)}\text{Se}/\text{Zn}_x\text{Cd}_y\text{Mg}_{(1-x-y)}\text{Se}$ -InP Quantum Cascade Structures for Emission In the 3 – 5 μm Range," *J. Vac. Sci. Technol.* **B**, **28**, (2010)
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