ZnCdMgSe as a Materials Platform for Advanced Photonic Devices: Broadband Quantum Cascade Detectors and Green Semiconductor Disk Lasers

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ZnCdMgSe as a Materials Platform for Advanced Photonic Devices:
Broadband Quantum Cascade Detectors and Green Semiconductor Disk Lasers

by
Joel De Jesus

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

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

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THE CITY UNIVERSITY OF NEW YORK
Abstract

ZnCdMgSe as a Materials Platform for Advanced Photonic Devices: Broadband Quantum Cascade Detectors and Green Semiconductor Disk Lasers

by Joel De Jesus

Adviser: Professor Maria C. Tamargo

The ZnCdMgSe family of II-VI materials has unique and promising characteristics that may be useful in practical applications. For example they can be grown lattice matched to InP substrates with lattice matched bandgaps that span from 2.1 to 3.5 eV, they can be successfully doped n-type, have a large conduction band offset (CBO) with no intervalley scattering present when strained, they have lower average phonon energies, and the InP lattice constant lies in the middle of the ZnSe and CdSe binaries compounds giving room to experiment with tensile and compressive stress. However they have not been studied in detail for use in practical devices. Here we have identified two types of devices that are being currently developed that benefit from the ZnCdMgSe-based material properties. These are the intersubband (ISB) quantum cascade (QC) detectors and optically pumped semiconductor lasers that emit in the visible range. The paucity for semiconductor lasers operating in the green-orange portion of the visible spectrum can be easily overcome with the ZnCdMgSe materials system developed in our research. The non-strain limited, large CBO available allows to expand the operating wavelength of ISB devices providing shorter and longer wavelengths than the currently commercially available devices. This property can also be exploited to develop broadband room temperature operation ISB detectors.

The work presented here focused first on using the ZnCdMgSe-based material properties and parameter to understand and predict the interband and intersubband transitions of its
heterostructures. We did this by studying an active region of a QC device by contactless
electroreflectance, photoluminescence, FTIR transmittance and correlating the measurements to
the quantum well structure by transfer matrix modeling. Then we worked on optimizing the
ZnCdMgSe material heterostructures quality by studying the effects of growth interruptions on
their optical and optoelectronic properties of devices. Growth interruptions improvements were
evident both by sharper PL peaks on multilayer structures and by narrow and more efficient
electroluminescence emission on intersubband devices. By using these techniques, and using
materials lattice matched to InP, we then developed the first II-VI based QC detector with high
responsivity for 3.5 and 2.5µm IR wavelengths, explored the combination of several detector
cores arrangements to make a broadband IR detectors, and achieved a QC broadband detector
operating from 3.3 to 6 µm also with high responsivity and high detectivity. For the visible
lasers, we have successfully combined distributed Bragg reflectors (DBRs) and resonant cavity
MQW structures into a single device to achieve green semiconductor disk lasers (SDL). We also
investigated novel strain engineered multiple quantum wells (MQWs) using CdSe and ZnSe
strained layers. This last research provided materials with shorter wavelength activity in the IR,
achieving absorption as low as 2.5 µm, and visible red emission lattice matched to InP, providing
new building blocks for all of the above mentioned devices. Our results demonstrate the
outstanding capabilities of the material system, and provide tools and techniques for further
development.
Acknowledgements

In the following paragraphs I will attempt to thank key persons that helped me through the work of this dissertation, knowing that I will leave some people outside just because failing memory. Excuse me for the ones I miss, but I will do my best to mention most of them.

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Chapter 1

Introduction

1.1 Introduction

Molecular Beam Epitaxy (MBE) is a thin film growth technique that enables the deposition of layers of crystalline materials with such quality and precision that one can construct highly sophisticated, complex devices that require very thin and precise layers in thickness and composition. Such precise layered structures are the basis for the explosion in electronic and photonic industries that affect virtually every aspect of modern life. These devices take advantage of specialized materials with unique properties that provide a wide range of functions and applications.

The ZnCdMgSe-based II-VI semiconductor materials are a novel type of materials that have unique properties that can target some applications that are not currently possible with other more well established materials systems. Some of those properties are having bangaps that cover the entire visible spectrum, especially the green, yellow and orange regions of the visible spectrum, which are not easily reached with other materials. This enables them to cover those areas of the visible spectrum where there are no direct lasers available. Also when these materials are used to form multilayered structures, their band alignments produce a large conduction band offset, which can enable the fabrication of intersubband devices that operate at wavelengths below 4.0 μm. Lower average phonon energies, which these materials also possess, may also produce devices that target gaps in the long wave IR and Terahertz regimes.

In this chapter we will describe the MBE technique, and how it applies to these materials. Then we will discuss the ZnCdMgSe material system itself. We will then present some
information about intersubband devices, followed by a description of semiconductor disk lasers, both of which can benefit from the ZnCdMgSe materials properties. We will end with a brief account of what we want to achieve with this dissertation.

1.2 Molecular Beam Epitaxy (MBE)

Figure 1.1: Schematic diagram of an MBE chamber

Molecular beam epitaxy (MBE) is an advanced, complex, well-established technology to grow epitaxial semiconductor thin films and multilayered structures. Its ability to control the growth with atomic layer accuracy has proven to be useful to make heterostructure devices based on precise thickness cavities (for VECSELs) and bandgap engineering based on multi-quantum wells (MQW) for intersubband devices such as quantum cascade (QC) lasers and detectors. The MBE process achieves epitaxial growth in an ultra-high vacuum environment through the chemical reaction of one or more thermal molecular beams with a crystalline surface of the substrate. The UHV environment is achieved by the use of several pumps used in sequence (such as diaphragm, turbomolecular, cryo and ion pumps). Prior to the material growth the MBE chamber walls are also cooled with liquid nitrogen, which further maintains the clean UHV
environment for high quality material growth. Fig. 1.1 shows a schematic view of the principal components of an MBE chamber.

The molecular beams are provided by heating up ultra-pure (6N to 8N) source material in a crucible inside a thermal Knudsen effusion cell. Typically, elemental sources of the elements that make up the desired material are used. For example, to deposit GaAs one uses a Ga source and an As source. The temperature of each cell can be used to control the flux of the chosen atomic or molecular species. The values of the fluxes are obtained by measuring the beam equivalent pressure detected by an ion pressure gauge (flux gauge) placed at the substrate position. The alloy composition of the desired epilayer is controlled by controlling the flux ratio of the elemental beams. The chamber is designed so that the fluxes from all the cells intersect at the substrate. Each cell has a shutter between the cell and the substrate. This permits abrupt interruption of the beam flux to the substrate, enabling to start and to stop the deposition and/or doping. The substrate temperature can also be varied to control dynamical processes taking place at the surface. These include atomic diffusion, adsorption, re-evaporation and nucleation, to name a few. The crystal growth rate is kept high enough that surface migration of the specified species in the surface is ensured giving rise to a crystalline layer with low defect density and high purity. [1, 2]

All of the MBE experiments described in this thesis were done in a Riber 2300P dual-chamber system. In it, two MBE chambers dedicated to the growth of II-VI and III-V materials, respectively, are connected by a set of ultra-high vacuum transfer modules which we call the “track”. The III-VI chamber is equipped with Ga, In, Al, As, Si (for n-type doping) and Be (for p-type doping) cells. The II-VI chamber is equipped with Zn, Cd, Mg, Se, Te, ZnCl₂ (for Cl flux for n-type doping) and a radio frequency (RF)-plasma assisted nitrogen cell for p-type doping.
Prior of inserting new substrates into the loading chamber the molybdenum blocks are cleaned thoroughly first with HCl to remove indium remaining from the previous substrate bond, bromine/ methanol solution to remove any deposited II-VI or III-V materials, and *aqua regia* (HCl:HNO$_3$) etch, which removes a very thin layer of the Molybdenum, exposing a perfectly clean surface. Once clean, the epi-ready substrates are mounted to the Mo blocks using melted indium to attach the substrate to it.

The substrate of choice for all the samples in this work was InP (001). The composition of all the constituent layers needed for each device structure was previously calibrated so the layers would be closely lattice-matched to the substrate. In our MBE system, one chamber is used to deposit III–V materials; in this case an InGaAs buffer layer grown after the removal of the native oxide surface layer from the InP substrate. The InGaAs buffer layer produces an atomically smooth surface with the desired As-termination, which has been proven to improve the quality of the II-VI films. [3] The other MBE chamber was used to grow the II–VI layers, specifically a nearly lattice-matched Zn$_x$Cd$_{1-x}$Se and Zn$_x$Cd$_y$Mg$_{1-x-y}$Se alloys. Prior to the II-VI materials growth on InP substrates, special techniques have been developed in our laboratory to ensure a smooth and nearly defect free III-V to II-VI interface. Once the InGaAs/InP sample is in the II-VI chamber, exposure to a Zn flux during 30 seconds is done [4] prior to growth of a low temperature ZnCdSe buffer [5]. Both of these steps have been proven to reduce defects.

The growth of the materials and the substrate oxide desorption were monitored in-situ by reflection high energy electron diffraction (RHEED). In RHEED, an electron gun sends high speed electron beam at a glancing (very low) angle to the surface of the substrate. The glancing angle ensures very low penetration of the beam into the sample so that the information it provides is mainly from the surface. RHEED diffraction can tell us information of surface
arrangement, the film growth procedure, and from the oscillation of the principal electron beam reflection (specular reflection), the growth rates of the materials being deposited. RHEED oscillations on calibration samples were used to obtain accurate growth rates for each material before a structure is grown. Typical MBE growth conditions for the II-VI materials were a substrate temperature of 270 °C and a Se-to-group II flux ratio of ~ 6. This gave rise to Se-stabilized growth conditions. Growth rates were about 0.4 µm/hr for the lattice matched ZnCdSe, and 0.8 µm/hr for a lattice matched Zn$_{x}$Cd$_{y}$Mg$_{1-x-y}$Se alloy with a 2.85 eV bandgap.

1.3 The ZnCdMgSe-based materials

![Figure 1.2: Bandgap versus Lattice mismatch to InP for the ZnCdMgSe family of materials.](image)

The MBE group in The City College of NY has demonstrated that Zn$_{x}$Cd$_{y}$Mg$_{1-x-y}$Se based semiconductor materials can be grown lattice matched to InP substrates with extremely high quality and low defect densities. Figure 1.2 shows the bandgap of this material, as a function of lattice mismatch to InP (001), a useful substrate to consider for these materials. [6]
The vertical dotted line at 0% mismatch to InP indicates all the possible alloys of these materials that can be grown lattice matched to this substrate. The lowest bandgap lattice matched material is a Zn\textsubscript{x}Cd\textsubscript{1-x}Se ternary alloy with a bandgap of 2.1 eV. By adding MgSe into the lattice matched ZnCdSe ternary, the resulting lattice matched quaternary material has a bandgap that can be varied from 2.1 eV to 3.6 eV. This large tunable bandgap extends over the visible spectrum from the orange up to the UV. In all our lattice matched structures, we used the lattice matched ZnCdSe as our material for the wells, and a higher bandgap ZnCdMgSe alloy as the barrier material to make the quantum wells. Quantum wells emitting throughout most of the visible spectrum range could be obtained from these QWs by simply adjusting the QW thickness.

[7] Our group has also previously shown that we can successfully dope these materials n-type incorporating Cl to the lattice [8], and that 80% of the bandgap discontinuity lies in the conduction band, leading to a large and tunable conduction band offset (CBO) as high as 1.12 eV.[9]

The calculated bandstructures of II-VI selenides [10, 11], and experimental measurements of CBOs [9] confirm that this system has favorable properties to make intersubband devices to cover the near, mid, and long-wavelength IR ranges. It has a lattice matched CBO\textsubscript{MAX} of ~1.1 eV, and the Γ and X valleys are distant, promising no intervalley carrier scattering even when strained. Based on these results, we have recently reported quantum well infra-red photodetectors (QWIPs) [12, 13] operating at room temperature. In this thesis we will present results of quantum cascade detectors (QCDs) [14] operating in the 3-5 µm range, as well as broad band QCDs.

From Figure 1.2 we can also see that the InP lattice constant lies midway between the two extremes of the ZnCdSe alloy curve and divides the quaternary ZnCdMgSe material plane.
roughly into two halves. This suggests that one can design strain into the materials and obtain strain compensated structures by combining layers with compressive and tensile strain. This greatly expands the possibilities of bandstructure engineering for this material system. Strain has been previously used, with great success, in InGaAs/InAlAs QC lasers to expand the operation wavelength of the devices [15, 16].

1.4 Intersubband transitions and devices

![Schematic bandedge profile of a ZnCdSe/ZnCdMgSe QW](image)

Figure 1.3: Schematic bandedge profile of a ZnCdSe/ZnCdMgSe QW. Conduction band (CB), valence band (VB), the bandgap energy (Eg), the conduction band offset (ΔEc), the electron bound states (e1, e2) and the heavy and light holes bound states (hh1, lh1) are shown. The bandgap is actually more than 7 times larger than the intersubband transition.

When ultra-thin layers of materials (below 16 nm) are sandwiched between larger bandgap ones, quantum confinement effects manifest themselves by producing discrete energy levels for the electrons in that band, instead of the continuum bands present in bulk
semiconductors. In the direction parallel to the quantum well plane, every band in the semiconductor is split into discrete higher values of energies. If the conditions are right (enough band offset, and appropriate width of the quantum well) more than one discrete level can form from any given band, and particles can now populate these allowed energy states. Transitions between these discrete states are called intersubband (ISB) transitions. Fig. 1.3 illustrates schematically what is meant by an ISB transition. These transitions usually lie in the infrared regime, and they have become the building blocks of a broad range of infrared optoelectronic devices.

When a thin material with a lower bandgap $E_g$(well) is sandwiched between a higher bandgap material $E_g$(barrier) a quantum well for electrons can be formed in the conduction band, or one in the valence band for holes, or both, depending on how the bands align in these materials. The value of the conduction or valence band offsets can be determined experimentally. Let us focus now in the cases where there is a quantum well formed in the conduction band, and the material is doped with electrons (n-type). In this case we need to only consider what happens in the conduction band. If for a given conduction band offset (CBO), one changes the thickness of the well, at very thin values we have only one bound state. As the well gets thicker it can support two bound states, and so on. In the cases where two or more bound states are present, the energy difference between the first exited state and the ground state reaches a maximum value as we change the well thickness, and then decreases as the well is made even thicker. This means that the energy of the transition (and therefore the wavelength of its ISB transition) is determined by the thickness of the well layer rather than by the bandgap of the materials. This enables one to tailor the detection or emission wavelength of this transition over a wide range using the same heterostructure material.
When quantum wells are brought together they will feel the perturbation of the adjacent ones. There is certain barrier thickness where no interaction is felt. The barrier thickness of interaction depends on the effective mass of the electron in the barrier. Below a certain thickness, the QWs interact with each other and the principles of perturbation theory apply, splitting all the degeneracies, and shifting the energies from their unperturbed value. In fact, quantum wells interact similar to the way atoms do, having discreet energy values, splitting their values if degenerate when brought close to each other, and creating bands (mini-bands) when enough of them are combined. [17]

Furthermore, there is a polarization selection rule that applies to ISB transitions: only light polarized along the growth direction can induce them. Also, the selection rules for ISB transitions are different than those for interband transitions. The probability of an interband transitions in a QW is given by the overlap integral of the wavefunctions, therefore in a totally symmetric system, there can be e1-h1 transitions (transition from the first electron state to the first heavy-hole state) but no e1-h2 transtion. In ISB transitions it is the momentum overlap, or the overlap integral of the final function with the derivative of the starting one that matters. Therefore in a completely symmetric case we can have transitions e1-e2, but not e1-e3. These latter selection rules are lifted when the symmetry is broken, and although not totally forbidden, some transitions become stronger than others. [18]

This understanding helps us construct systems by bandgap engineering, using multi-quantum well structures grown by MBE. This has made possible the demonstration of unipolar ISB devices such as the quantum well infrared photodetector (QWIP) [19], the quantum cascade (QC) laser [20] and the QC detector [21]. Some of these devices are commercially available operating in the mid to long-infrared wavelengths (4 – 14 µm) and have many applications in
science (spectroscopy), medicine (non-invasive glucose monitoring), environment (monitoring of trace pollutants), industry (process monitoring) and military (countermeasure). All of these areas and possibly others would benefit if these devices could be made to work at shorter wavelengths (i.e., 1.4 - 3 µm). The ZnCdMgSe materials system can help us achieve this wavelength range.

The most commonly used material system for ISB devices is the AlGaAs/InGaAs alloys grown on InP. That lattice matched system has a conduction band offset (CBO) of 0.52 eV [22], not enough to achieve the 6-5 µm range. Larger offsets can be obtained when strained layers are used, CBO_{MAX} ~ 0.7 eV. This CBO is enough to cover the short wave IR, but devices made from those structures do not reach 3 µm due to intervalley scattering [23, 24]. This is so because the Γ and X valleys change their energy values when strained. The Γ-X crossover point dictates when a material goes from direct bandgap to indirect, changing drastically the material properties. This crossover limits the maximum CBO that can be reached. Therefore the limiting factors to achieve shortwave IR wavelengths (< 4 µm) are maximizing the CBO, while avoiding intervalley scattering.

The desire to make ISB devices in the 2-4 µm wavelength range has created the need for other material systems. In this thesis we show that the MBE grown ZnCdMgSe-based system is suitable for these applications by optimizing their growth conditions, developing mid-IR ISB devices, and exploring new “strain engineered” structures for their shorter wavelength operation.

1.5 Semiconductor Disk Lasers

Another device that can benefit from the properties of the ZnCdMgSe system are the semiconductor disk lasers (SDL). Even though the idea of optically pumped SDLs has been
around for a while [25] it was not until the 1990s that the concept was adapted into working devices [26, 27, 28].

A SDL is basically an efficient light emitter whereby, when optically pumping a semiconductor gain structure that lies inside an external optical cavity, vertical laser emission of the semiconductor structure can be achieved. SDLs are also known throughout the literature as optically pumped vertical external cavity surface emitting laser (VECSEL) or optically pumped semiconductor lasers (OPSL). Conceptually, they are very similar to a solid state laser, with the difference that the emission wavelength in a solid state laser is defined by fixed optical transitions in the chosen material, while in a SDL the emission wavelength can be engineered by the composition and width of the QWs used.

Even though the optical pumping and external cavity makes the design of SDLs more complex than injector edge emitters, the possibility of upscaling of the area while the gain remains single mode, and the possibility of inserting several gain structures in the same cavity [29], are two examples in which the output power can be enhanced while maintaining great beam

Figure 1.4: a) Diagram of the components of a SDL (or VECSEL) operation, b) zoom-in of the SDL structure.
quality, which may be difficult to achieve in injection devices. Therefore these devices are important to make very powerful and compact laser sources. The external cavity also enables the incorporation of non-linear components to allow ultra-short pulse operation. Furthermore, their operation does not require doping, making them simpler to grow and avoiding doping limitations of many materials systems.

The design of a conventional SDL is like a half-vertical cavity surface emitting laser (VCSEL), where the top mirror is missing. [30] Fig. 1.4 shows a schematic of a typical SDL device. First we have the substrate, which many times has the undesirable property that it can absorb the photons produced by the active region. To eliminate absorption by the substrate, it is necessary to grow a mirror structure on top of it, before the active emitting region of the SDL is grown. Such a mirror can be a stack of 1/4 wavelength thick layers of different refractive index (the greater the difference the better) to create a distributed Bragg reflector (DBR). The DBR should be >99.99% reflectance to the emitted light in order to enable lasing of the SDL. After growing the DBR we are ready to grow the gain medium. For it we need to grow an absorber layer that must have a bandgap resonant with the pumping laser wavelength to assure maximum absorbance of the beam and the most production of electron-hole pairs. Light production is made in quantum wells, which are placed in a periodic gain arrangement between the absorbing layers. In these types of devices the transitions occurring in the quantum wells are interband transitions, from valence band holes to conduction band electrons. We then complete the structure with a top window layer.

Research on SDLs is focused mainly in three topics: power scaling, generation of ultrashort pulses, and extending the wavelength coverage. Our work with the ZnCdMgSe-based alloys is addressing the last topic. The 530–630 nm wavelength range (pure green to orange) is
particularly interesting as it cannot be reached via direct emission from other lattice-matched semiconductor structures. SDL lasers are available from the near-infrared (2\(\mu\)m) to shorter wavelengths up to the visible red using InP and GaAs based semiconductors. Blue lasers are available with GaN, and InGaN is currently being used to push the GaN materials towards the long wavelength emission, but this material system is still in development. Non-linear effects in semiconductors are also used to generate lasers within that gap, in which infrared radiation is converted to visible light via two phonon absorption. But non-linear processes are of second order, and thus low in intensity. Therefore the realization of first order (direct) light production from semiconductor structures can provide lasers with higher power than the non-linear ones.

The ZnCdMgSe-based system has been shown to cover the entire visible spectrum, filling the gap from green, yellow, and orange that still exists in direct emission from other semiconductors. In this dissertation we will discuss the preparation of SDL structures, targeting to cover the visible green range.

1.6 Scope of this dissertation

The overall scope of this dissertation is to show that ZnCdMgSe materials grown by MBE are ready to provide useful devices that are needed to fill some fundamental property gaps. For this we have optimized the material quality by incorporating growth interruptions during growth and have demonstrated QC detectors operating over a broad mid-IR region and developed SDLs that emit in the green. We have also incorporated strained layers to provide bright red emission and near-IR active ISB materials lattice matched to InP, showing that we can further expand the wavelength coverage of all these devices.
After this introduction in Chapter one, in the second chapter we will describe all the experimental setups and techniques that were used for this research. We will explain the experiments with details and describe our numerical modelling techniques.

Chapter 3 presents the study of quantum well structures used in the active region of QC lasers using a technique known as contactless electroreflectance (CER) to characterize the three coupled QW design for the QC laser active region.

In chapter 4 we will discuss our experiments to improve to optimize the material deposition, and enhance its quality and the effect of the improvements on QC laser performance. Specifically, we improved the interfaces between the many layers of our multi-layered structure. We implemented growth interruptions of 20 seconds during which the sample was only exposed to a selenium flux. This led to improvements of the optical properties and the device performance when implemented.

Chapter 5 investigates the potential of the ZnCdMgSe material system to make strained quantum wells with ZnSe and CdSe. In this work we pushed this material to the limit in terms of applying strain and deposited the materials with the largest lattice mismatch within the ZnCdMgSe system to make quantum wells for near to mid IR activity. High quality structures were achieved by strain compensation.

In chapter 6 we present the realization of quantum cascade detectors made from ZnCdMgSe materials. Both single band detectors and broadband detectors with quality that surpass those of the best available QCDs were obtained.

In chapter 7 we describe our results and materials developments towards the realization of semiconductors disk lasers. Bright green emission and lasing from edge emitting cavities were demonstrated.
As a whole, our results demonstrate that the ZnCdMgSe system has great potential for the production of workable and useful devices that fulfill needs not achievable from conventional materials currently in use. Finally, I will conclude my thesis discussion with proposed future work, presented in Chapter 8.
Chapter 2
Experimental techniques and theoretical simulations

2.1 Introduction

Most of the research in this dissertation has been focused on working with instrumentation and techniques to perform experiments that take us from growing materials and structures for devices, to the materials physics and understanding. In this chapter we will discuss those experiments in some detail, giving some theoretical background, and description of their process. First we will discuss the most important technique in our laboratory: the molecular beam epitaxy (MBE) materials growth technique, by which all our samples and devices are made. After that we will discuss the characterization techniques used to study the structural, optical, and electrical properties of the semiconductors and devices. The results of these characterization measurements are to relate the materials physics and device properties to their physical properties.

Simulations or numerical calculations were also needed in order to interpret and understand many of the results. Specifically, we solved the time independent Schrodinger equation numerically for systems of quantum wells made with the ZnCdMgSe-based materials grown by MBE. Those methods are discussed at the end of this chapter.

2.2 MBE growth procedure

2.2.1 Pre-MBE growth preparation

Before the MBE growth there are a number of steps needed in preparation. First, we need to clean the blocks and mount on them the substrates to have them available for the deposition.
The blocks are the substrate holders used to handle the samples during growth. We mount the substrates to them to be able manipulate them within the MBE system. Blocks are made of molybdenum, and since material is deposited on them during growth, every time they are used they must be cleaned thoroughly to keep the epitaxial process as clean as possible.

The molybdenum block cleaning process is as follows. Using clean plastic or Teflon tweezers, the blocks are first dipped into hydrochloric acid (HCl) to remove the indium used to glue the substrate previously used there. After the indium is completely removed, we rinse the blocks thoroughly with D.I. water. Then, we dip them in methanol to remove all the water prior to dipping them into a bromine/methanol solution. This step etches all the III-V and II-VI semiconductor material from the blocks. After we leave them there for 10 minutes, we rinse each block with methanol, to remove all the bromine, and rinse them with water. Then *aqua regia* is prepared by mixing Hydrochloric Acid and Nitric Acid in the ratio of 1:1, and by dipping the very top surface of the blocks and rinsing them quickly with D.I. water, we etch away the top molybdenum layers in the blocks to expose a new surface. The blocks are rinsed for 10 minutes in D.I. water to make sure all the aqua regia is diluted and completely rinsed. We then remove water from the blocks by placing them in an ultrasonic bath for 10 minutes while covering them with methanol. To end the cleaning process, the blocks are blown dry with nitrogen gas, and then stored in a clean petri-dish.

Once the blocks are cleaned, we are ready to attach the substrates to them. Sometimes substrates have to be treated with solvents or acids to prepare their surface prior to growth. In our case we have no need to prepare the substrates before deposition, since we purchase epi-ready substrates (from AXT Company). The substrates just need to be cleaved and glued to the molybdenum blocks. An ingot of high purity (6N) indium metal (the same kind used to load the
indium cell crucible) is used to bond the substrate to the molybdenum block. A small piece of indium (about 1mm³) is more than enough. A hot plate is heated to about 160ºC, close to the melting point of indium. The indium is melted in the very center of the block, and spread drawing a shape as close to the shape of the substrate that is going to be used. We place the substrate piece on the indium melt and move it back and forth and side to side, for at least a minute. This ensures that a uniform film of In is there to allow for good thermal contact with the block, as well as securing it in place. Once we make sure the indium has stuck on the back of the substrate, we remove the block with the substrate from the hot plate. Before the block is completely cold (but not when it is too hot) all the excess indium extending outside the substrate must be removed using metal tweezers and a blade, leaving only indium beneath the substrate. Once this is done, the substrate and block are covered, allowed to cool down, and we are ready to insert them into the loading chamber. All this process of cleaning the blocks and bonding of the substrates is done in a class 100 laminar flow clean hood. Then the substrates are inserted onto a cart in the loading chamber, the only part of the MBE system that gets regularly exposed to atmosphere. When the pressure is right, we then transfer the cart with the blocks and substrates to the interior part of the track, which always kept at high vacuum.

The day of growth we start by filling the cryopanels of the chamber with liquid nitrogen, this will traps molecules on the walls of the chamber and let us reach better ultra-high vacuum conditions. After an hour of liquid nitrogen flow we start raising the cell temperatures, and once the cell temperatures are set, we wait for the temperatures to stabilize (50 minutes for the III-V chamber and 60 mins for the II-VI chamber). We then measure the fluxes from all the cells that we are using. The flux of each elemental cell is related to the composition of the alloy grown. During the flux measurement step we can confirm the proper operation of the shutters, and we
can assess if the material in the cell is becoming depleted, etc. Once the fluxes are measured, we set the final temperatures of the cells based on these fluxes and previous calibrations. At this point we are ready to start growing material.

2.2.2 Growth in the III-V chamber

First I will describe the steps that take place in the MBE chamber that it is used exclusively for the deposition of III-V materials. In the III-V chamber we remove the native oxide of the InP substrates and deposit InGaAs alloy lattice matched to InP as a buffer layer. The substrate is inserted in the III-V chamber and the holder placed in the growth position. The substrate temperature is raised slowly until 200°C, at which temperature the main shutter and Arsenic shutter are opened. Prior to the oxide desorption, RHEED screen inspection will show a uniform cloudy pattern indicating an amorphous surface from the oxide. We continue to raise the temperature, inspecting the RHEED screen, until we begin to see faint rods in the screen. Around 400°C, we slow down the rate of raising the temperature to 10°C steps, since we are approaching the oxide desorption of InP and we do not want to overshoot it. It is important to know exactly when we desorb all the oxide to quickly lower the temperature, because the oxide desorption temperature is higher than the phosphorous desorption temperature on InP. Failure to lower the temperature immediately after the oxide desorption occurs will damage the surface by the creation of indium droplets, resulting in defects in the films grown on top of them. The best way to monitor this point of complete oxide desorption is by the RHEED [31, 32], where the surface goes from a 2x4 (As-stabilized) reconstruction to a 4x2 (In-stabilized) reconstruction. (see discussion of the RHEED in section 2.3 of this chapter) When the substrate temperature is around 350°C the RHEED pattern of the InP surface will start showing the ½ order surface
reconstruction pattern in the [110] direction. As we reach the 500ºC, this pattern will become very diffuse, until it disappears, and when the oxide is completely removed, a ¼ order surface reconstruction appears (indicative of an In-rich surface) in the same direction. Immediately when we see this change, we bring down the temperature 30ºC from the oxide desorption temperature, and when it stabilizes we start the growth of the InGaAs layer by opening the gallium and indium shutters (arsenic was open all the time through the oxide desorption process).

The moment we start the InGaAs growth, the RHEED pattern turns spotty, indicating that the first InGaAs layers on the InP substrate exhibits 3D growth. With time (approximately 1.5 minutes) we observe that the pattern recovers to a streaky (2x4) pattern, indicative of a 2D growth or layer by layer growth mode. For the usual growth of the InGaAs lattice matched to InP, the flux of gallium is around $9.0 \times 10^{-8}$ torr, the flux of indium is $2.0 \times 10^{-7}$ torr, and the flux of Arsenic is $1.3 \times 10^{-5}$ torr. In other words, the flux ratios are $F_{\text{In}}/F_{\text{Ga}}=2.22$, $F_{\text{As}}/(F_{\text{In}}+F_{\text{Ga}})=43$. The excess arsenic is known to help stabilize the growth. These parameters give us a growth rate of ~0.81 μm/hr, value in agreement with the XRD thickness fringes from the InGaAs layer, and cross sectional SEM measurements.

We let the InGaAs film grow to the desired thickness (usually 9 more minutes). To stop the InGaAs growth, we close the indium and gallium shutters, leaving the arsenic shutter open. Immediately after closing those two shutters, the temperature is set to 100ºC, this will stop the current flow thru the substrate heater, and the substrate temperature will begin to drop. We wait until the substrate temperature drops 100ºC from the growth temperature to close the arsenic shutter and the main shutter. When we reach 100ºC in the substrate heater, the sample is ready to be taken out of the III-V chamber and inserted in the track cart to be transported in vacuum to the II-VI chamber.
The InGaAs layers can also be doped n-type with silicon atoms, or p-type with beryllium atoms. The temperature of the cells for the appropriate doping must be calibrated by Hall Effect measurements. At the end of the day, we lower the cell temperatures, keeping Al at 400°C, Ga and In at 200°C (keep them melted), while arsenic, Si and Be cells are brought down to 25°C, and the liquid nitrogen flow is stopped.

2.2.3 MBE growth in II-VI chamber

When the sample is transferred into the II-VI chamber, all the shutters must be closed at this moment, including the main shutter to ensure that no deposition takes place on the sample surface during the transfer. RHEED screen inspection lets us know the status of the InGaAs buffer layer prior to deposition. The pattern that is observed at this time is a (2x4) pattern with the center line missing in the ¼ order reconstruction. The substrate temperature must be set to 180°C. At that point we perform a surface treatment to minimize the stacking fault density caused at the III-V to II-VI interface. We start by a zinc exposure, for which we open the zinc shutter, and then the main shutter, irradiating the InGaAs surface for 30 seconds. The RHEED pattern during the Zinc irradiation should not noticeably change from the initial (2x4) InGaAs reconstruction. We then immediately open the cadmium and selenium shutters, to grow 10 nm of ZnCdSe alloy lattice matched to InP at this relatively low temperature. The RHEED pattern now changes to the typical (2x1) pattern of Se-rich II-VI materials growth. After the ZnCdSe low temperature buffer layer is grown, we close the zinc and cadmium shutters, and leave the selenium shutter open. While the sample is under a selenium flux we increase the temperature of the substrate to 300°C, which is our optimum growth temperature for II-VI layer growth. When
the temperature stabilizes, we are ready to start growing the desired II-VI material structure, or bulk layer.

The usual growth rates for ZnCdSe are 0.4μm/hr, and those of ZnCdMgSe vary based on the desired bandgap (determined by the Magnesium content) from 0.6 to 1.0μm/hr. The cadmium to zinc flux ratio for lattice matched ZnCdSe is $F_{\text{Cd}}/F_{\text{Zn}}=2.1$, and it varies for ZnCdMgSe depending on the desired bandgap/Mg composition. We have noticed that Magnesium containing alloys prefer to grow at slightly higher temperatures than the ZnCdSe alloys, but a temperature at which both materials grow well is chosen to facilitate the growth of complex quantum heterostructures. Selenium is the excess species during growth, and we maintain a selenium to group II ratio $F_{\text{Se}}/F_{\text{Cd}}+F_{\text{Zn}}>5$. When we finish growing the structure, we close all the shutters except the Selenium and the main shutters. We then reduce the substrate temperature to 200°C. When we reach ~240°C, we close the selenium shutter and the main shutter to avoid excess selenium on the surface. When the substrate heater cools, we are ready to take out the sample. If we are finished with growth for the day we lower all the cell temperatures to 25°C, we stop the flow of LN$_2$, and open all the shutters keeping the main shutter closed.

2.3 In situ surface characterization: Reflection high energy electron diffraction (RHEED)

The MBE chamber is equipped with an electron gun and a phosphorous screen at opposite sides. They are positioned in such a way that the electron beam is incident on the substrate surface at a very low angle. Since the stability of electron beams require vacuum, the MBE conditions of ultra-high vacuum environments make it possible for electron diffraction techniques to be used simultaneously with growth. Thus reflection of high energy electron
Diffraction (RHEED) is an in-situ characterization technique that we have available, and we use it to monitor the growth in real time. A diagram of the RHEED setup is shown in Fig. 2.1.

In RHEED electrons are accelerated by a voltage of the order of 10-20KV, and the beam hits the sample at a very low glancing angle (~2°), therefore the beam mostly interacts with the 2-dimensional plane of atoms at the surface, and the diffraction pattern displayed on the screen gives information mostly of the sample surface. The RHEED diffraction patterns depend on the atomic arrangement, the flatness of the surface, the composition at the surface, and the orientation between the beam and surface [33].

From RHEED we learn about the nature of the crystal growth. If we see streaks (rods) in the pattern we can say that the growth is happening in 2D or layer by layer mode (nearly atomically flat), which is the preferred way to grow good quality multilayers with very flat and smooth surfaces. Other features that can appear in the diffraction pattern are spots. A spotty pattern is indicative of a 3D or island growth. That is, the surface is rough with protruding clusters of material that diffract the beam into spots. This is usually indicative of non-optimal growth conditions, and if kept up for too long, will lead to the evolution into polycrystalline...
material. Polycrystalline material can be seen in the RHEED screen as diffuse rings. Sometimes no diffraction pattern is observed, the screen is hazy or cloudy. This occurs when the surface we are observing is dominated by amorphous material, as is the case when the native oxide on the substrates surface is present.

![Diagram of (001) GaAs (2x4) As terminated surface.](image)

Figure 2.2: a) Diagram of (001) GaAs (2x4) As terminated surface. RHEED patterns for b) an un-reconstructed surface (principal lattice) b) a 2-fold reconstruction, and c) a 4-fold reconstruction.

Surface reconstructions observed in RHEED refer to the rearrangement of surface atoms to accommodate the dangling bonds in the very top layer. As we discussed earlier, during the III-V materials growth we typically see a pattern along the [110] azimuth in which the principal lattice streaks are separated into a two-fold pattern, while along the [110] the principal lattice streaks are split into a four-fold pattern, resulting in a (2x4) surface reconstruction. This (2x4) reconstruction is typical for As-rich (001) InGaAs surface [34]. It comes about by the formation of surface “dimers” in the well-known “missing dimer configuration, illustrated in Figure 2.2. During the II-VI material growth under the typical Se-rich conditions we see a two-fold pattern along the [110] azimuth, while along the [110] direction we see an unreconstructed (1-fold) pattern, resulting in a (2x1) surface reconstruction. This (2x1) reconstruction is typical for a Se-rich (001) ZnSe surface [35]. If the III-V growth is carried out under Ga-rich conditions, the
surface reconstruction becomes (4x2), while for the II-VI under group-II rich conditions, an C(2x2) reconstruction is observed. Thus, the surface reconstruction pattern gives us information about the chemical termination of the surface that is present during growth.

Another feature of the RHEED is that it allows us to get accurate information about the growth rate of the materials [36]. When the electron beam hits the surface, most of it is reflected and produces a bright spot along the 0th order diffraction rod, which is called the specular reflection. If we measure the intensity of this specular reflection, we will see that its intensity oscillates as a function of time. These intensity oscillations are related to the layer-by-layer growth occurring on the surface. When the surfaces are flat at the end of a full monolayer growth, the intensity of the specular spot is maximum. When the layers are forming, the surface is only partially covered and these scattering centers diffuse the beam, and therefore decrease the intensity of the specular spot. An intensity oscillation from a maximum to the next maximum indicates the formation of a full monolayer (ML). A direct growth rate in ML/s can be obtained from the oscillations plot. Since we know the lattice constant of our materials (made to be lattice-matched to InP) we can then obtain the growth rate in μm/h or nm/s. Electron diffraction measurements of the layer thicknesses are used to corroborate these growth rates with high accuracy. Since many of our structures require the growth of very thin layers with precise thickness control, it is very important to measure these growth rates each day so we can calculate the amount of time needed to grow a specific material.

2.4 Post-growth characterization techniques

2.4.1 X-ray diffraction (XRD)
X-Ray diffraction is a very useful, non-destructive characterization tool by which many parameters from a crystalline material can be obtained, such as its lattice constant, alloy composition, structural arrangement, parameters of a superlattice, strain in the material, thickness of embedded layers, etc.

A crystalline material is one in which atoms are arranged in a lattice with high symmetry, in a long order repeatable structure. The materials used in this study (ZnCdMgSe-based layers on InP substrates) have a cubic structure, in specific a face centered cubic structure with two atoms as its basis. This atomic arrangement is known as a zinc-blende structure. The numerous parallel planes of atoms in the lattice, create a diffraction grating to any wave that has wavelength in the order of the separation between these inter-atomic planes. X-rays are photons of high energy (125eV-125KeV) that have wavelengths in the order of 0.01-10nm. Since the wavelength of X-rays is in the order of the inter-atomic spacing in crystals, diffraction occurs, in which X-rays scatter, and interfere constructively or destructively producing a diffraction pattern.

The relation for a fully constructive interference by X-rays passing thru these planes of atoms is given by Bragg’s law (which is visualized in Fig 2.3), which states that for the X-rays to interfere fully constructively the path difference between the planes must be a multiple of the wavelength:

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

Here \(d_{hkl}\) is the distance between planes \(d_{hkl}=a/(h^2+k^2+l^2)^{1/2}\) (a is the lattice constant), h, k and l are the Miller indices of the corresponding (hkl) plane, \(\theta\) is the Bragg angle, and \(\lambda\) is the wavelength of the incident X-rays.
In order to achieve close lattice matching our materials with the InP substrate (required for high quality of thick layers) high resolution of the X-ray measurement is needed to resolve the epi-layer and substrate peaks. To achieve high resolution, the x-ray source is monochromatized using the diffraction of a high quality crystal as the X-ray source, and the beams are collimated onto the sample. An additional dispersion of the beam is done with another crystal, usually called analyzer crystal, before the diffracted beams from the sample hit the detector [37, 38].

When several layers are repeated multiple times in a structure, the superimposed periodicity by the repeated layer sequence induces superlattice peaks to appear near the lattice reflection. These superlattice peaks are caused by the additional diffraction grating in the growth direction. A series of equally-spaced satellite peaks associated with this superlattice shows in the spectrum. From the superlattice peaks the thickness of the group of repeated layers (i.e., the period of the superlattice, \( d_{SL} \)) can be obtained. To calculate the period we use the following approach.

Let \( m \) and \( n \) be two diffraction orders from the same superlattice, and \( \theta_m, \theta_n \) their corresponding Bragg angles. Then from Bragg’s law we have:

![Figure 2.3: Diagram used to derive the Bragg’s Law used in X-Ray diffraction](image)

\( \theta \)

\( \theta \)

\( d \)

\( d \sin \theta \)
\[ 2d_{\text{SL}} \sin \theta_m = m \lambda \]
\[ 2d_{\text{SL}} \sin \theta_n = n \lambda \]

To consider the two peaks, by subtracting these two equations, we obtain:

\[ d_{\text{SL}} = \frac{\lambda (m-n)}{2(\sin \theta_m - \sin \theta_n)} \]

We usually get several (sometimes more than 10) superlattice peaks, so to consider all of them, we calculate \( d_{\text{SL}} \) for sequential peaks, and then take an average of all of them. For superlattice peak sensitivity, X-ray reflections that are more nearly parallel to the surface of the sample are more effective. Therefore sharper and more well-resolved superlattice peaks are obtained for (002) scans than for (004) scans.

X-ray scans can sometimes also exhibit thickness fringes [39, 40]. These fringes indicate a high crystalline quality of the layer, and very sharp interface. We typically observe them for the thin InGaAs layers, which provides evidence of a good substrate for the II- VI crystal growth.

The perpendicular lattice mismatch (which in the case of a fully relaxed will be the same as the parallel mismatch and to the actual lattice mismatch between the epi-layer and the substrate) is given by

\[ \frac{\Delta a}{a_s} = \frac{(a_i - a_s)}{a_s} \times 100\% \]

Which, by using Bragg law becomes:

\[ \frac{\Delta a}{a_s} = \left[ \frac{(\sin \theta_s / \sin \theta_L)}{\sin \theta_L} - 1 \right] \times 100\% \]

\( \theta_s \) and \( \theta_L \) are the Bragg angles from the substrate and the layer, respectively.

For the work described in dissertation all films or device structures where grown on (001) oriented substrates, and so perpendicular mismatch can be obtained by doing a 2\( \theta \)-\( \omega \) coupled scan near any plane parallel to (001), like (002) or (004) scans. Most of our samples were thick enough to be relaxed (at least 1um or more), therefore typically we consider the perpendicular
mismatch as the actual mismatch of the sample. For strained layers, the mismatch must be obtained by doing additional asymmetric scans. All the XRD measurements made here were made using an X-ray diffractometer (Bruker D8 Discover) with an analyzer crystal for high resolution.

2.4.2 Photoluminescence (PL)

Photoluminescence (PL) is a non-destructive technique that provides information about the most fundamental optical properties of materials [41-43]. Information such as bandgap, quality of samples or structures, composition, donor and/or acceptor states, deep defect levels and spin processes (when polarized light is used) can be obtained. The instrumental setup is relatively simple compared to other characterization techniques. PL can be described as a three step process, 1) excitation of carriers by laser light, 2) thermalization of the carriers, and 3) recombination by radiative or non-radiative processes. These are illustrated in Figure 2.4 for the case of a direct bandgap semiconductor.

When a sample is excited with light having an energy higher than the material’s bandgap then electrons in the valence band can absorb the impinging photons energy, and be promoted to empty states in the conduction band, creating an electron-hole (e-h) pair. The excited e-h pair will relax non-radiative losing some energy towards quasi-thermal equilibrium distribution, a process called thermalization. Then the thermalized e-h pairs recombine by several process shown in figure 2.4. For direct bandgap material, like the ones described in this thesis, this recombination is mostly radiative, yielding photons that can collected and detected.
The PL spectra can be rich with different features coming from different types of transitions. High quality intrinsic materials usually only have conduction band to valence band or excitonic radiative recombination. When the material is doped with p-type and n-type dopants, secondary emission peaks may be due to donor to valence band or conduction band to acceptor transitions, and when both bound states are present, donor to acceptor transition may be seen.

Deep level emission is sometimes seen when material defects are present. Defects states are present within the bandgap of the material and usually are seen as a broad PL band. Most often, deep levels emission indicate poor quality material, not desired for devices, since their presence decreases the lifetime of carriers and their luminescence efficiency.

In a direct bandgap material, the conduction and valence band minimum are aligned on top of each other in the same momentum scale, therefore a transition between them can happen with no change of momentum. This implies that they have high rates for photon emission.
(radiative transition). These materials are preferred for the fabrication of lasers or other optoelectronic devices, like the ones discussed here.

Since at thermal equilibrium the carrier population decreases exponentially with energy, the emissions are strongest from the lowest energy states. As a result luminescence near room-temperature is a sensitive probe of low-lying energy levels only. For bulk samples PL was used mainly to obtain the bandgap energy of the material, and in MQW samples it was used to obtain the transition from the conduction and valence ground states due to quantum confinement. To measure exited states we rely on modulation spectroscopy techniques that will be discussed later. Quality of the material, sharpness of the QWs interfaces, and thickness uniformity from MQWs samples can be probed measuring the FWHM of the PL emission peaks.

The steady-state PL studies discussed in our work were carried out at room temperature and at 77K by optically-pumping the samples using the 325 nm He-Cd laser line with ~30 mW of output power. The laser radiation was incident at ~45° to the sample surface normal. The luminescence from the surface was collected and the spectra analyzed by a spectrometer (Ocean Optics HR2000).

2.4.3 Scanning electron microscope (SEM)

Electron microscopy relies in the interactions of high energy electrons with matter to image or analyze samples. Electrons are sent perpendicular to the sample surface, and they can go thru the sample and be transmitted and/or undergo elastic or inelastic scatterings. From these interactions they can produce secondary electrons, backscattered electrons, Auger electrons, Bremsstrhunng (continuous) X-rays, characteristic X-rays, visible light, phonons, electron-hole pairs, etc.
In the scanning electron microscope (SEM) there are no transmitted electrons, and the particles that are detected are the backscattered electrons or the secondary electron emission to image the surface, and the characteristic X-rays to get spectroscopic information about the composition of the material (elemental analysis). Even though our SEM is equipped with all of this, in this thesis we only used the SEM to obtain images with the secondary electrons. The SEM setup that we used produced electrons from a field emission source. This is more convenient than the filaments sources, since field emission electrons have a narrower energy distribution, and therefore gives better resolution.

For SEM measurements, samples must be conductive. A path for the electric current from the imaging surface to the sample holder base must be available for discharge. Non-conducting samples tend to accumulate the electrons and get charged easily and therefore are coated with very thin gold/platinum or carbon films to provide this conductive channel. If an area of the sample becomes charged, more electrons are ejected from there, creating bright spots. Since our devices and samples are mostly grown on semi insulating substrates, the samples tend to charge easily. To compensate for that, large adjustments lowering the brightness and contrast were made to obtain good images.

The electron gun in the SEM sends a fine beam of electrons that are accelerated (5-20 keV) and sent thru a series of electromagnetic condenser and objective lenses that focus and raster the beam through the sample. Secondary electrons are low energy electrons (>50eV) that are produced by knocking out of other electrons by inelastic scattering with the primary electron beam. Since they are not that energetic (cannot penetrate deep), secondary electrons comes from near the surface of the sample, therefore collecting them and using their counts and the position of the raster to create an image will create an image that is a good representation of the surface.
For the semiconductors grown in our lab, narrow band materials or highly doped materials usually show with lighter colors, because their higher density of free electrons, the ones with higher bandgap usually show darker ones. The SEM was mostly used to image the cross sections of our devices to measure the thickness of the layers. Samples are cleaved right before inserting them into the microscope to protect the cross-sectional area from oxidation or contamination with dust particles. Then the sample is placed in a sample holder that will make the fresh cleaved side to point up, enabling the image of the cross-section. The cross-section electron microscope images in this work were recorded using a field emission SEM (Zeiss Supra 55 VP).

2.4.4 Contactless Electroreflectance (CER)

Contactless electroreflectance, similar to photoreflectance, is a modulation spectroscopy technique applied to reflectance.[44, 45] Even though reflectance spectroscopy can pick up details of optical transitions from the joint-density of states, the reflectance spectrum can be broad and smooth with a large background signal, so that some optical transitions can be missed. Modulation spectroscopy produces a derivative like spectrum in which the background is
subtracted, and optical transitions can be pinpointed with great detail, even for measurements at room temperature.

The CER setup is shown in Fig. 2.5, and the experiment consists of a simple reflectance setup in which we use a white light lamp, which is passed through a monochromator, focused, and made to strike the sample surface; the reflected light is then focused onto a detector. The modulation of the electric field is applied in the sample holder, where a high AC voltage is supplied across the sample, which is held between a copper back contact and a metal mesh in the front of the sample (to let light pass thru). The metal mesh is at a small distance from the sample surface, separated by a dielectric spacer. The sample geometry creates a small capacitor, within which the sample is placed. This high field (1KV) is AC sent with a frequency set at 1 KHz. This frequency is also fed to the lock in amplifier as the reference signal. Thus the sample feels this modulated field and any signal that originates from the sample is also modulated.

Once the spectrum is recorded, we can fit it with differentials of Lorentzian or differentials of Gaussian line shapes to find the optical transitions. These fitting functions are varied according to the nature of the critical point that we are observing (changes for bulk, QWs,
or QDs transitions) so some knowledge of the sample is needed to analyze the data. Once the fit is done, quantum mechanical modelling is used to identify all the transitions.

In quantum well structures, CER room temperature measurements yield a spectrum that is richer in information than the ones obtained by room temperature photoluminescence (PL). In PL, we can only extract information about the lowest energy transitions, while with CER we can obtain information about all the higher energy transitions as well. As with PL, the CER technique is nondestructive and requires no sample preparation for measurements.

2.4.5 Time resolved Photoluminescence

Time resolved photoluminescence (TRPL) spectroscopy is a technique used to investigate the carrier dynamics in semiconductors. TRPL basically records the PL intensity by a streak camera as the intensity decays or evolves as a function of time after the sample is excited by a short pulse of light. The measurement of this time delay is repeated many times and averaged to account for the statistical nature of the PL emission. From fitting this response we can obtain values for the carrier recombination lifetime $\tau$. We used the technique to quantify the quality of our materials, since more non-radiative processes can be available by defects, shortening the lifetime of the PL, and to distinguish between several emissions processes such as spontaneous and stimulated emissions in laser samples.

In our experiments, TRPL measurements were carried out at room temperature using the second harmonic radiation (400 nm) of a femtosecond Ti: sapphire laser and chirped pulse regenerative amplifier system (Spectra-Physics Spitfire). The laser system generated light pulses of 130 fs full-width-at-half-maximum (FWHM) duration, at a repetition rate of 1 kHz. The laser beam was incident on the sample at an angle of 45° to the surface normal, and the PL from the
surface was collected in the back-propagation geometry along the normal to the surface by an optical fiber connected with the streak camera (Hamamatsu streak scope C4334). The streak camera temporal resolution is limited to 20 ps. A 50 lines/mm grating was used in the spectrometer to observe the spectrum from 400 nm to 600 nm. The pump power of the second harmonic at 400 nm was measured by a power meter (Spectra-Physics Model 407A).

2.4.6 Transmission electron microscope (TEM)

Transmission Electron Microscopy (TEM) is a technique that allows us to image the crystalline structure of our materials by obtaining images of it with very high magnification. It sends high energy electrons through a very thin sample and creates an image with the electrons that pass through the specimen. It uses an electron gun to provide electrons, accelerate them and pass thru a series of electromagnetic lenses to create a small beam striking the sample. Electrons that go thru the sample are then passed thru another series of lenses to be projected into a screen. The technique relies on the density of electrons around an atom to make an image. These larger density atoms will scatter the impinging electrons, creating darker areas.

This imaging technique requires that the samples be very thin, therefore special sample preparation is required to image our samples by TEM. Sample preparation involves mechanical polishing, dimpling, ion milling, and/or focused ion beam. The samples are then placed in a TEM grid, usually a mesh made of copper, and then inserted in the microscope.

In our case, we did not do the sample preparation, nor the imaging. We used the services of Evan Analytical Group for this. We used TEM only in the chapter #5 where we made structures with ZnSe and CdSe materials, in order to investigate whether we were forming
quantum wells or quantum dots during the growth of these materials. TEM provided enough resolution to do this investigation.

2.4.7 FTIR absorption spectroscopy

Since the energy scale of intersubband (ISB) transitions lies in the infrared, in order to obtain direct information about them from the grown structure, we perform Fourier Transform Infra-Red (FTIR) transmittance experiments.

An FTIR spectrometer does not use dispersive techniques (such as grating spectroscopy) in which individual wavelengths are spread and scanned. FTIR spectrometer uses all wavelengths at the same time. It creates an interferogram of the light passing thru the sample using a Michelson interferometer, and then calculates the Fourier transform of the interferogram to obtain the spectra. Figure 2.6 shows a block diagram of the FTIR spectrometer. Conventional instruments have the sample and detector inside the box of the spectrometer, but in our case we modify this by taking the sample compartment and detector outside of the spectrometer box. This is needed because of the multiple pass geometry used to measure our ultra-thin samples.

The heart of the FTIR spectrometer is the Michelson interferometer. A beam splitter sends half of light to a fixed mirror, and the other half to a moving mirror, then they are combined again and sent through the detector, where the intensity is measured as the path length is changed.

The ISB absorption was measured using a Nicolet Nexus-670 FTIR spectrometer with a polarizer and a liquid-nitrogen cooled HgCdTe detector. Since TM or p-polarization couples to the ISB transition, while TE or s-polarization does not, and the surface reflection loss of the incident light is the same for both orthogonal polarizations, the absorbance for the sample is
obtained by taking the negative natural logarithm of the p-polarized transmittance over the s-polarized transmittance.

Special care has to be taken when choosing the lenses. We have CaF\textsubscript{2} and ZnSe lenses available in our laboratory. CaF\textsubscript{2} lenses transmit from 180nm-8.0\mu m, and ZnSe lenses transmit from 600nm-16\mu m. But even though ZnSe lenses transmit further into the mid-IR (larger range), CaF\textsubscript{2} lenses have more transmittance % of light than the ZnSe lenses in the range in which they overlap. For this reason we decide to use CaF\textsubscript{2} lenses when dealing with samples of short wavelength, like the ones discussed in chapter 5, which extend into the near IR. For samples that have activity further into the mid-IR we use the ZnSe lenses, for example for the QC laser structure studied in chapter 4.

Since the films that create the quantum structure that interacts with IR are thin films (several microns), they will have low absorption when light goes through the film only once (Beer’s Law). Therefore to enhance the absorption we create a multipass geometry. In that geometry the beam passes through the thin film structure several times, enhancing the absorption. To make this multipass geometry sample we need to polish the sample into a bar.
with 45 degree facets at the ends, making this characterization technique destructive. We use clear optical wax to hold the samples to the metal pieces used to hold them to polish.

### 2.5 Quantum Wells simulations

To solve the one dimensional (1D) time independent Schrödinger equation (SE) for the calculation of the bound energy levels in a system of quantum wells we used the transfer matrix method (TMM) [46], which is described below.

Using the effective mass approximation, the time independent 1-D SE for a particle with mass $m^*(x)$ in a potential $V(x)$ is:

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

The wavefunctions used for the $j^{th}$ layer were:

$$\Psi_j(x) = A_j \cos(k_j x) + B_j \sin(k_j x) \text{ (in wells)}$$

$$\Psi_j(x) = A_j e^{k_j x} + B_j e^{-k_j x} \text{ (in barriers)}$$

The corresponding boundary conditions used were:

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

$$\frac{1}{m^*_{j-1}} \frac{d}{dx} \Psi_{j-1}(x_{j-1}) = \frac{1}{m^*_j} \frac{d}{dx} \Psi_j(x_{j-1})$$

$A_j$ and $B_j$ are the coefficients, and $x_{j-1}$ is the point at the boundary between the two layers.

The boundary conditions are applied to the wavefunctions, 2x2 matrices are obtained relating each coefficients at a given boundary, and then they are all used to relate the first ($A_0$, $B_0$) and last ($A_N$, $B_N$) coefficients as:

$$\begin{bmatrix} A_N \\ B_N \end{bmatrix} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \begin{bmatrix} A_0 \\ B_0 \end{bmatrix}$$
Now, since the amplitude of the wavefunctions should be zero as \( x \) tends to plus or minus infinity, this implies that exponentials coefficients in the first and last barrier are 0, and this relates that \( M_{22}(E) = 0 \), where \( E \) is the eigenvalue. Here lies the simplicity of the TMM that instead of several coupled fundamental equations, we just end with one. Even though, \( M_{22}(E) = 0 \) is not an easy equation and it is solved numerically by varying \( E \). Non-parabolicity effects are also considered by changing the value of \( m^* \) for both materials as \( E \) changes as:

\[
m^* = m_0^*[1 + (E - V)/E_g]
\]

We used the TMM in chapter 3 to solve the three coupled quantum well structure of the active region in our QC lasers. The material parameters will be given there. The other quantum wells simulations done to design the QC lasers on chapter #4, the QC detectors on chapter #6, and the ZnSe/CdSe strained QWs on chapter #5 were done with an updated version of Erwin Jr. [47] package software, using our materials parameters.
Chapter 3

Characterization of a triple asymmetric coupled quantum wells structure for components of intersubband devices

3.1 Background and motivation of the three coupled quantum wells study

Coupled quantum wells are essential to make intersubband devices based on Quantum cascade (QC) technology, like the QC lasers and QC detectors. These devices have applications that currently expand within the environmental, scientific, industrial, communication, medical and military sectors. In order to further investigate the intersubband capabilities of the ZnCdMgSe-based II-VI semiconductors, here we bring three quantum wells together to explore the effects of their coupling. The quantum wells are deep and wide enough for each one of them to have two bound states, and this configuration is frequently used as quantum cascade lasers active regions, but as we will discuss in chapter 6, these ended being the active region of our first QC detector, therefore understanding its behavior is very relevant to this work. As QC lasers active regions, those made of the ZnCdMgSe-based material system would help push the operating wavelength of these devices to lower wavelengths. The II-VI material system consisting of ZnCdSe/ZnCdMgSe lattice matched to InP is a good candidate because it can offer a CBO as high as 1.12 eV, much larger than that the commercially used material system of InGaAs/InAlAs.

In this chapter we introduce a non-conventional way to characterize intersubband devices and structures called contactless electroreflectance (CER). CER is an electric-field modulated reflectance measurement technique. [44, 45] In quantum well structures, CER measurements enable us to measure the band to band (or interband) optical transitions. In these kinds of
structures the CER spectrum is richer than the photoluminescence (PL) one. In PL, we can only extract information about the lowest energy transitions, while with CER we can obtain information about excited state transitions as well. CER yields derivative like spectra with reduced background and sharp features that can be observed even at room temperature. Additionally, the CER technique is non-destructive and requires no sample preparation for measurement.

Intersubband devices like QC lasers and detectors rely on the precise growth of materials to create a complex multilayered structure that is engineered so that the quantum confinement of the charge carriers produces a specific arrangement of available energy levels. The energy levels are designed in such a way that when the device is biased with a certain voltage IR radiation is emitted due to ISB optical transitions. We show that CER can be used to predict the available energy levels, and thus the ISB transitions in the structure. Measurements of ISB transitions can be done with Fourier transform infra-red (FTIR) spectroscopy, but unlike CER, this requires destructive sample preparation [18].

CER has been used in our laboratory to measure the conduction band offset of the ZnCdSe/ZnCdMgSe heterostructures [9], and to characterize the optical transitions in multiple quantum well structures [48]. It also enabled us to characterize double asymmetric quantum well (2ACQW) structures [11, 49] used in the active region of QC lasers. Here we use CER to characterize a more complex active region design consisting of a triple asymmetric coupled quantum well (3ACQW) structure. These active regions are used in the designs of mid-IR [50] and terahertz [51] QC lasers. The advantages of a 3ACQW active region design over a 2ACQW is that the 3ACQW requires a lower operating electric field, enhancing the tunability of the lasers.
[50], and the two optical phonon relaxation makes it easier to depopulate the lower lasing level to the injector.

Here we will study in detail a 3ACQW structure designed to be the active region of a QC laser with CER. This will require us to identify the optical transitions in the system by solving the quantum mechanical problem involving the QWs numerically. Then this knowledge we will use it to predict the behavior of a more complex structure, the actual intersubband device, the QC laser.

Figure 3.1: Layer diagrams of the 3ACQW test structure and the quantum cascade laser structure. Notice that both structures share the same active region.
3.2 Growth and characterization

MBE Sample growth: The samples were grown by MBE in a dual chamber Riber 2300P system, as described in chapter #2. Four samples were grown and characterized for this work: a ZnCdSe bulk calibration sample, a ZnCdMgSe bulk calibration sample, a QC laser structure (sample # A3195) and a 3ACQW test structure (sample # A3196). The samples were grown sequentially to keep the growth conditions similar. The calibration samples and the 3ACQW test structure were grown on (001)-oriented semi-insulating Fe-doped InP substrates. The QC laser structure was grown on a (001)-oriented n-type (~2 x 10^{17} cm^{-3}) Si-doped InP substrate. The InGaAs buffer was undoped for the calibration samples and the test structure, and n-type doped for the QC laser structure.

Figure 3.1 shows a schematic of the structures of the 3ACQW test structure and the QC laser structure. The QC laser structure has a core region that consists of injector and active regions repeated 40 times, sandwiched between two n-type doped ZnCdSe thick layers and topped by a heavily n-type doped ZnCdSe contact layer. The test structure consists of 20 repeats of the active region, separated by 11nm thick ZnCdMgSe barrier layers and capped by a thin ZnCdSe layer. The designed thicknesses of the QC laser core, starting from the injector, is 10/20/10/18/12/17/14/16/16/15/20/36/8/30/9/26 (repeated 40 times), with the ZnCdSe wells indicated in bold, the ZnCdMgSe barrier in italic, and the Cl-doped (n~3x10^{17} cm^{-3}) layers are underlined. The active region is composed of the last three wells in the core, shown in italics. The designed thicknesses of the 3ACQW test sample layers are 110/36/8/30/9/26 (repeated 20 times). All of the above thickness values are given in angstroms.

HR-XRD measurements were done using a Bruker D8 Discover X-ray diffractometer with a Cu source (\(\lambda = 1.54056\)). High resolution 2θ-ω measurements were made along the (004)
reflection of InP to determine the perpendicular lattice mismatch and the period of the superlattice structure in the growth direction. Photoluminescence (PL) measurements at room temperature were made using the 325 nm line of a He-Cd laser, a PMT detector, lock-in amplifier and a monochromator. CER measurements were taken at room temperature. The fitting of CER spectrum using derivatives of Lorentzian lineshapes,[52] was performed by means of the WinPR program version 2.1. The sample was polished prior to the FTIR absorption measurements, in order to obtain a multi-pass geometry before the measurements. The ISB absorption was measured using a Nicolet Nexus-670 FTIR spectrometer with a polarizer and a liquid-nitrogen-cooled HgCdTe detector. Since TM or p-polarization couples to the ISB transition, while TE or s-polarization does not, and the surface reflection loss of the incident light is the same for both orthogonal polarizations, the absorbance for the sample is obtained by taking the negative natural logarithm of the p-polarized transmittance over the s-polarized transmittance.

The 3ACQW structure was modeled solving the one-electron, one dimensional Schrodinger equation numerically using the transfer matrix method (TMM).[46] A Matlab program was used to obtain the values of the energy of the bound states of the electrons in the conduction band and those for the light and heavy holes in the valence band. It also gave the modulus square of the wavefunctions (example of its output is shown in Figure 4). Lowest order approximation for band non-parabolicity was included using a two band model. The energy levels for the electrons and the light and heavy hole are given in Table 3.1.

The ZnCdSe parameters used in the calculations are: spin orbit splitting ($\Delta_0$)=0.442 eV, bandgap ($E_g$)=2.10 eV, $m_e^*$=0.128me, $m_{hh}^*$=0.56me, $m_{lh}^*$=0.11me, where me is the rest mass of the electron. The ZnCdMgSe parameters are: $E_g$=2.93 eV, $m_e^*$=0.181me, $m_{hh}^*$=0.67me,
\(m_{lh}^* = 0.22m_e\). Other parameters used here from the combinations of these materials are:

\(Q_c (= CBO/E_g) = 0.82\), CBO = 0.681 eV, valence band offset (VBO) = 0.149 eV. All these parameters were taken from M. Muñoz et al. [9] and references therein. The notation used is: \(e^#\) for electronic states in the conduction band, \(h^#\) and \(l^#\) for the heavy hole and light hole states, respectively, in the valence band, where \(#\) indicates the order of the state, starting with 1 for the ground state, 2 for the first exited state, and so on.

### 3.3 Results and discussions

Figure 3.2 shows the HRXRD 2θ-ω scans along InP (004) reflection of the 3ACQW test structure (a), and the QC laser structure (b). The designed period for the 3ACQW test sample is 21.9 nm, while the calculated period obtained from the XRD satellite peaks separation is 22.0 nm, showing an excellent agreement. For the QC laser structure, the designed period is 27.7 nm and the measured one is 27.2 nm, again showing a very good agreement. This indicates good control of the growth parameters, and confirms that our samples are very close to their design.
The overall crystalline quality of the samples is good as evidenced by the sharp peaks observed in the HR-XRD, with the 3ACQW test sample slightly better than the QC laser structure. The lattice mismatch calculated using the zeroth order superlattice peak is 0.19% for the QC laser structure, and 0.05% for the 3ACQW test structure. This larger lattice mismatch in the QC laser might be one of the factors contributing to its lesser quality.

The PL data of a ZnCdSe bulk calibration sample, a ZnCdMgSe bulk calibration sample, and the 3ACQW test structure are shown in the lower section of Figure 3.3. The PL of the ZnCdSe sample has a peak at 2.10 eV, as expected for lattice matched ZnCdSe [11]. The ZnCdMgSe PL has a peak at 2.93 eV. Using the reported value of the parameter Qc=0.82 for our material system[9], the CBO in the structures is expected to be 0.68 eV. Ref. 53 reports a spin-orbit splitting for the InP lattice matched ZnCdSe to be Δ₀=0.442 eV. Using this and the
measured value of the bandgap, we obtain that $E_g + \Delta_0 = 2.542$ eV. The PL spectrum of the 3ACQW test structure gives us information of the ground state transition (e1-h1) of this system, with a peak at 2.23 eV.

The top of figure 3.3 shows the room temperature CER spectrum of the 3ACQW test structure. The experimental data is shown by the solid line. A fit to the data was obtained using the derivatives of a Lorentzian lineshapes. The fit is superimposed on the data by the dashed line. Excellent agreement was obtained between the fitted curve and the experimental data. The arrows in the figure point to the 10 transitions needed to obtain a good fit. The energy values of those transitions are: 2.106, 2.229, 2.281, 2.325, 2.373, 2.504, 2.656, 2.773, 2.903, and 2.920 eV.
From the PL spectra of the calibration samples we identify the 2.106 eV transition as the ZnCdSe cap bandgap, the 2.504 eV transition as the ZnCdSe $E_g + \Delta_0$, and the 2.903 eV as the ZnCdMgSe barrier bandgap. From the PL spectrum of the 3ACQW test structure we can also identify the 2.229 eV transition as the e1-h1 transition, the ground state transition of the 3ACQW sample. To identify the remaining transitions we have to rely on numerical calculation solutions of the 3ACQW system using the TMM.

Figure 3.4: TMM calculation results for the electrons in the conduction band (positive values) and the holes in the valence band (negative values) of the 3ACQW test structure, with a value of zero assigned to the top of the valence band of the quantum wells. Plotted are the moduli square of the electronic wavefunctions obtained from the TMM analysis.
By performing TMM calculations of the 3ACQW structure we obtained the energy values of the bound states for electrons in the conduction band (Table 3.1), and the light and heavy hole in the valence band, as well as the moduli square of the wavefunctions (Figure 3.4). Using individual confinement energy values, the electron-hole transition energies were calculated. Even though the asymmetry of the system relaxes the selection rules, making all the transitions possible, we used the moduli square of the wavefunctions to predict the more probable interband transitions (to compare them with the CER measurements) and the most probable ISB transitions (to compare them with the FTIR absorption measurements).

The comparison between the values obtained from PL and those calculated using TMM are shown in Table 3.2. The experimental values are in excellent agreement with the ones predicted by the model, confirming good control of the growth of the 3ACQW sample and

<table>
<thead>
<tr>
<th>Conduction band bound states (eV)</th>
<th>Valence band bound states (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_1 = 2.2013$</td>
<td>$h_1 = -0.0230$</td>
</tr>
<tr>
<td>$e_2 = 2.2378$</td>
<td>$h_2 = -0.0317$</td>
</tr>
<tr>
<td>$e_3 = 2.2833$</td>
<td>$h_3 = -0.0429$</td>
</tr>
<tr>
<td>$e_4 = 2.4826$</td>
<td>$h_4 = -0.0930$</td>
</tr>
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<td>$e_5 = 2.5937$</td>
<td>$h_5 = -0.1225$</td>
</tr>
<tr>
<td>$e_6 = 2.7030$</td>
<td>$h_6 = -0.1492$</td>
</tr>
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</table>
supporting the validity of our assignments. We further conclude that the TMM calculations provide a good model for the QC laser active region.

The CER and TMM analyses were performed on the 3ACQW test sample, which contains the active region of the QC laser device. Figure 3.5 shows the FTIR absorption spectrum of the QC laser structure. We observe strong absorbance of photon energies at 272, 297, 380 and 416 meV. Using the TMM model results from the test sample we identified the

<table>
<thead>
<tr>
<th>CER fit (Exp.)</th>
<th>PL (eV)</th>
<th>TMM (Calc) (eV)</th>
<th>Assigned Transition</th>
<th>Difference (Exp. – Calc.) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.106</td>
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<td>2.1</td>
<td>ZnCdSe Eg</td>
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</tr>
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<td>2.229</td>
<td>2.23</td>
<td>2.2243</td>
<td>e1-h1</td>
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<td>2.3-h3</td>
<td></td>
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<td>2.6-l1</td>
<td></td>
<td>0.0232</td>
</tr>
<tr>
<td>2.773</td>
<td>2.7728</td>
<td>2.7-l2</td>
<td></td>
<td>0.0002</td>
</tr>
<tr>
<td>2.903</td>
<td>2.8520</td>
<td>2.9-h6</td>
<td></td>
<td>0.051</td>
</tr>
<tr>
<td>2.920</td>
<td>2.93</td>
<td>2.930</td>
<td>ZnCdMgSe Eg</td>
<td>-0.010</td>
</tr>
</tbody>
</table>

Table 3.2: Summary of the experimental CER fit results, PL measurements, and the calculated TMM energy values for the assigned transition. The last column is of the difference between the CER fit experimental value and the TMM calculation result.
observed transitions in the FT-IR spectrum of the QC laser structure as e1-e4, e3-e5, e2-e5, e3-e6, respectively. The calculated numerical values for these transitions are 281, 310, 356, 419 meV. We conclude that the calculations based on the CER measurement of the simplified test structure can accurately describe the transitions observed in the actual device structure. Small discrepancies between the measured transitions in the QC structure and the values predicted from the analysis of the test structure can be attributed to the effect of the injector region, and its perturbation to the energies. From these results we can predict the emission wavelength of the QC laser, which in this case would be at ~ 281 meV or 4.4 µm.
3.4 Conclusions

We grew a 3ACQW test structure and a QC laser structure made from ZnCdSe/ZnCdMgSe multilayers lattice matched to InP substrates, and verified by HRXRD that the grown samples resembled closely the layer design. We characterized the test structure using CER to measure the available energy levels and used PL measurements and a quantum mechanical model based on the TMM to identify all the measured transitions. FTIR absorption of a full QC laser structure, fabricated with the same active region design as the test structure, was also measured. The FTIR absorption transitions were identified using the results of the test sample characterization. We conclude that the CER measurements made on a simpler test structure consisting only of the active region of a QC laser allows us to accurately predict the behavior of the full, more complex QC laser device. We also conclude with these experiments that we have the correct parameters and accurate ways to simulate the quantum well systems made of ZnCdMgSe-based materials.
Chapter 4

Interface improvement by the incorporation of growth interruptions

4.1 Introduction

The growth of a working device is not easy because of all the parameters that must be considered. One such parameter we need to monitor is the lattice mismatch of the materials with respect to the substrate. Thick layers, such as cladding and wave guiding layers, for example, if they are strained will relax, leading to defects. Material quality has to be kept high, large densities of defects will produce midgap levels that will produce low energy transitions that lower the bandedge emission intensity and introduce deep levels in photoluminescence. For devices in which specific energy levels are designed to have specific transitions, these other available defect levels are detrimental because they provide more scattering centers and other pathways for charge to become inactive. Keeping adequate doping concentration throughout the structure is also crucial. Most intersubband devices are based on the conduction of electron through them, so proper doping will keep the electron concentration through the structure and keep conductivity high. Also appropriate doping is needed to populate the active quantum wells in the devices where an optical transition is expected to happen between the bound ground state and the first exited state in the conduction band. We have to make sure that the ground state level is populated with electrons for this to occur. Interface roughness is another scattering mechanism that exist in quantum well systems and multilayered devices [54]. It can detune the tunneling between wells, which could make a device not work. It can also broaden the linewidth of emitted light from the QW. Interface roughness, is the parameter we addressed with this series of experiments on the use of growth interruptions. Lattice mismatch and doping levels are taken care by careful calibration of the materials.
Growth interruptions are known to reduce the surface roughness on the growth of the 
AlAs/GaAs [55], AlGaAs/GaAs [56, 57], and in AlGaN/GaN [58]. This effects have mostly been 
quantified by reduction of the FWHM in PL spectra, but also by direct TEM observation [59] of 
the interfaces. Even though most of the literature shows that growth interruptions are beneficial, 
there are also reports where no effects are obtained with their use [60]. Also when growing on 
highly strained systems, interruptions in the growth are known to make the material condense 
into clusters or islands, increasing the roughness of the film. These effects of growth 
interruptions are widely applied to the production of quantum dots [61-63] and are known as 
quantum dot formation and “ripening”. In this chapter we explore the effects of growth 
interruptions on the MBE growth of our II-VI structures and devices. This is the first time 
growth interruptions have been used with these materials systems. The discussion that follows 
presents the results we obtained by their implementation.

4.2 Experimental Details

A total of four samples were growth in our dual chamber MBE system to investigate the 
effect of growth interruptions. Two samples were composed of a multi-QW structure that 
consisted of 11nm of a 3.0eV ZnCdMgSe layer lattice matched to InP, followed by a 2nm 
ZnCdSe layer lattice matched to InP. This two layers were repeated 20 times, ending with an 
additional 11nm ZnCdMgSe layer, and a 10nm ZnCdSe cap layer. These samples will be named 
MQW1 and MQW2, where MQW1 was grown continuously without growth interruptions, and 
in MQW2 we added a 20 second growth interruption between each layer. The other two samples 
where QC laser structures without cladding layers that are grown to test the electroluminescence 
of the structures. The layer sequence in angstroms for one period of this QC structure was, for
the active region: 20/36/8/30/9/26/10, followed by the injector region: 20/10/18/12/17/14/16/16/15, where the ZnCdSe layers are shown in bold, the ZnCdMgSe barriers are shown in italics, and the ones underlined ones indicate they are doped with the same ZnCl₂ cell temperature as the one used in a calibration sample where we obtained a carrier concentration of 3x10¹⁷ cm⁻³. These group of layers were repeated 40 times, and sandwiched between two thick ZnCdSe layers for top (450nm) and bottom contact (750nm). These QC structures are named EL1 and EL2, where EL1 was grown continuously without interruptions, while EL2 was grown with growth interruptions between all the layers in the active region layers (no interruptions in the injector). All these growth interruption are composed of 20s where all the shutters are closed, except the main and the selenium one, leaving a Se flux striking the surface. The effects of the growth interruptions were measured by doing XRD and PL experiments. To reach the PL emission of the active core in the ELs samples we etched the top ZnCdSe layer with a bromine/methanol solution.

4.3 Results and discussions

![Figure 4.1: a) HR-XRD 2θ-ω scans near the InP (004) Bragg reflections and b) photoluminescence spectra at 77K from the MQW1 sample (grown without growth interruptions) and MQW2 sample (grown using growth interruptions).]
Figure 4.1 shows the HR-XRD 2θ-ω scans near the InP (004) Bragg reflection and the PL spectra measured at 77K of samples MQW1 and MQW2. From the XRD scan we can clearly see that the sample that was grown with interruptions has sharper and more intense superlattice peaks, indicative of more abrupt surfaces. The PL spectra of the samples also show a peak width reduction for the sample that was grown with interruptions. The FWHM of the PL peak of the MQW1 sample is 45.1meV and for the MQW2 sample is 41.5meV. This reduction observed in PL peak width is consistent with observation of the XRD superlattice peaks sharpness. These experiments show the improvements on a simple quantum well structure. Next we tried these results on a more complex device structure.

Figure 4.2 shows the HR-XRD 2θ-ω scans near the InP (002) Bragg reflection and the PL spectra measured at 77K of samples EL1 and EL2. From the XRD scan we see a slight improvement in the superlattice peaks widths for the EL2 sample. From the 77K PL emission from the core of each sample we notice again that the one grown with growth interruptions is
narrower than the one without interruptions. The FWHM of the PL peak of the EL1 sample is 36.6meV, and the one from EL2 is 30.8meV.

EL1 and EL2 samples were sent to our collaborators at Princeton University and devices were fabricated (circular mesas with top and bottom contacts) from the samples grown, using standard lithography, wet etching, and metal evaporation techniques. The circular mesa is cleaved and electroluminescence emission spectra were measured from them.

Electroluminescence spectra measured at 80K were measured at several currents and are shown in figure 4.3. The electroluminescent results show a large difference between the two samples. The FWHM of the electroluminescence of EL1, grown without interruptions, was 641cm$^{-1}$, while in EL2, which was grown with growth interruptions, the electroluminescence FWHM was 358cm$^{-1}$, corresponding to a 45% reduction in linewidth. Sample EL2 is also a more efficient IR emitter, as we can see from the peak intensity at a particular driving current. Finally, room temperature electroluminescence (not shown) was only observed for the sample in which we...
used growth interruptions. From these results we can see that device performance even more noticeably enhanced by the use of growth interruptions.

4.4 Conclusions

In this chapter we presented the results of incorporating growth interruptions in the growth of simpler multi-quantum well structures, and in a quantum cascade electroluminescence device structures. From XRD scans we see improvements on the structural quality, from the PL measurements we see improvements on the optical properties, and from electroluminescence measurements we see large improvements on the device performance, all of these by performing growth interruptions in the samples.

Growth interruptions shows improvements by increasing the time of deposition. During the interruptions, it is expected that the atoms on the surface have time to diffuse and form a more atomically smooth surface. Since these experiments, we have implemented growth interruptions in every device sample that we grew, to take advantage of the improvements shown here.
Chapter 5

Strained compensated ZnCdMgSe/ZnSe/CdSe multi-quantum wells for short-wavelength intersubband transitions and interband red emitters lattice matched to InP

5.1 Background and motivation of ZnCdMgSe/ZnSe/CdSe MQWs

Quantum wells (QW) are the building blocks of intersubband (ISB) devices such as quantum well infrared photodetectors (QWIPs) [19], quantum cascade (QC) lasers [20] and QC detectors [21]. Commercially available ISB devices cover the mid-infrared wavelengths from 4 to 13 μm, and have many applications in science (spectroscopy), medicine (non-invasive glucose monitoring), environment (monitoring of trace pollutants), industry (process monitoring) and military (countermeasure). Achieving room temperature ISB activity shorter than 4 μm wavelengths, to expand their range, has been an area of research since the past decade. The commercially available ISB devices are made from the InGaAs/InAlAs alloys grown on InP. When lattice matched, this material system has a conduction band offset (CBO) of 0.52 eV [22], not enough to reach the 3-5 μm range. Larger offsets can be obtained when strained layers are used, but devices made from those structures have reached a short wavelength fundamental limit of ~4 μm, due to intervalley scattering [23, 24]. In order to achieve shorter IR wavelengths one must increase the CBO, while avoiding intervalley scattering. Some material systems have been investigated for shorter IR wavelength response, including, among the III-Vs, GaN/Al(Ga)N [64-66], InGaAs/AlAs/InAlAs [67, 68], InGaAs/AlAsSb/InP [69], InAs/AlSb [70, 71], and, among the II-VIs, (CdS/ZnSe)/BeTe [72, 73], and the ZnCdMgSe-based structures [74]. The last example is the focus of our current research.
Calculated band structures of ZnCdSe/ZnCdMgSe-based materials lattice-matched to InP [75, 11], and experimental measurements of their CBOs [9] confirm that this system has favorable properties to go beyond the commercially available wavelength range. It has a lattice matched CBO_max of ~1.1 eV, and the \( \Gamma \) and X valleys are farther apart than the III-Vs, promising no inter-valley scattering. With this system we have reported several novel results in ISB devices, including the first II-VI QWIP operating up to room temperature [13] and the first II-VI QC detector [76], with detectivities around 2.6 and 3.6 \( \mu \)m. Even though the maximum lattice-matched CBO is large enough to expand their operating wavelengths by simply using higher barriers and thinner wells, growth of high bandgap barrier materials, which require high Mg content, is difficult, and the materials are unstable to oxidation. Here we explore the use of the low bandgap CdSe material to make deeper quantum wells as an alternative approach.

Within the ZnCdMgSe alloy system, CdSe is the lowest bandgap binary at our disposal \( (E_g = 1.7 \text{ eV}) \). However, it has a large \( +3.5\% \) mismatch with our substrate of choice, InP. An approach that can be used to incorporate such a highly strained layer in a device structure is strain compensation. We will use ZnSe \( (E_g = 2.7 \text{ eV}) \) layers, which has \(-3.4\%\) mismatch to the InP as strain compensating layers. As long as the CdSe layers remain below their critical thickness on InP, estimated to be 10 ML, a similar amount of ZnSe can be deposited to achieve strain compensation on InP. ZnSe/CdSe quantum dots have been previously studied and grown on GaAs substrates, where the strain compensation approach for the growth of QWs cannot be easily applied. The optical properties of ZnSe/CdSe short period superlattices on InP have been reported [77, 78], but there are no reports of the use of the combination of these binaries to form isolated QWs.
In terms of interband devices emitting in the visible, our lab had produced red emitters before by adding Cd to the QW composition. For example, 650nm (1.90eV) red were obtained using Zn0.24Cd0.76Se strained quantum well \[79\], 630nm (1.96eV) red with a 10nm strained QW with lattice mismatch of 1.2\% \[80\], and 628nm (1.97eV) red with a 10nm strained QW with lattice mismatch of 1.8\% \[81\]. All of these structures were limited to only one quantum well, since they were highly strained. The production of thick structures, like intersubband devices, require the mismatch to be kept less than 0.2\% for them to grow \[82\]. Semiconductor membranes also require structures with none or low lattice mismatch, since the substrate release is detrimental to their processing \[83\]. Here we will report the first ZnCdMgSe-based II-VI red emitters that are strain engineered to be lattice matched to the InP substrate, therefore allowing their use in intersubband structures and SDL membrane applications.

In this chapter we will discuss the growth of multi-QW structures grown by Molecular Beam Epitaxy (MBE) using a ZnCdMgSe alloy with a bandgap of 3.0 eV, lattice matched to InP, as the barrier material, compressively strained CdSe as the well material, and tensile strained ZnSe for strain compensation, all grown on InP substrates. We will choose to sandwich the CdSe layer with two ZnSe layers to form a symmetric step QW system. The multi-QW structures grown exhibit PL that can be tailored from 1.7-2.1 eV and show narrow short IR wavelength ISB absorption peaks as low as 2.56 μm, all these measured at room temperature. Simulations based on these results confirm that these structures can be used to cover the 2-3 μm range.

5.2 Experimental details of growth and characterization of ZnSe/CdSe MQWs
The samples were grown in a dual-chamber MBE system on semi-insulating InP (001) substrates as described on the experimental techniques sections. The II-VI samples structure is as follows. First a 120 nm ZnCdSe layer was grown, followed by 110 nm of ZnCdMgSe. Then the ZnSe/CdSe/ZnSe symmetric step QW structure was grown, followed by a 9.2 nm ZnCdMgSe barrier layer. The deposition times (and therefore the thicknesses) of the ZnSe and CdSe layers were varied to explore the properties for different QW thickness and different strain. This set of 4 layers was repeated 35 times, to create a multi-QW structure. After growth of the multi-QWs, a 110 nm layer of ZnCdMgSe was grown. We capped the structure by growing a 10 nm ZnCdSe layer, to protect the Mg containing layers from oxidation. Brief growth interruptions of 10 s, during which the sample was only irradiated with a molecular flux of Se, were used at the interfaces between layers throughout the entire structure. The compositions of ZnCdSe and ZnCdMgSe were calibrated to ensure that they are closely lattice-matched to the InP substrate. No change of the cells temperatures was made after this calibration for the deposition of the ZnSe and CdSe compounds. RHEED oscillations were used to obtain growth rates, which were 0.38 µm/hr for ZnCdSe, and 0.80 µm/hr for the ZnCdMgSe layers. RHEED oscillations could not be observed for CdSe, therefore we will vary the deposition times of the CdSe and ZnSe layers to vary the QW thickness and strain. Information for the samples investigated here is given in Table 5.1, which includes deposition times used for the CdSe (tCdSe), the ratio between the tCdSe and the total ZnSe deposition time (tZnSe), and the samples characteristics.

Structural information of the grown samples was obtained by performing high resolution transmission electron microscopy (TEM), and X-ray diffraction (XRD). The electron microscope used was a Hitachi HD2700 scanning transmission electron microscope (STEM) with spherical aberration correction. It was operated at 200kV acceleration voltage. Dark field
transmitted electron images were acquired in atomic number contrast mode (ZC) detected with High Angle Annular Dark Field (HAADF) detector.

Steady-state PL and Fourier Transform infrared (FTIR) absorption measurements were performed to investigate the optical properties of the structures. To obtain the anticipated energy values for the FTIR absorption the symmetric step QW was simulated and the Schrodinger equation for the electron solved using a one-band conduction band model with an energy dependent effective mass that accounts for non-parabolicity, and pseudo-potential parameter to account for strain.

### 5.3 Results and discussions

TEM images of sample 2 are shown in Fig. 5.1. In the low magnification image on the left we see the full structure described earlier. The InP substrate is at the bottom, followed by the InGaAs and ZnCdSe buffer layers. Although the contrast between the InGaAs and ZnCdSe is
low, the interface could be identified (marked by arrows in the figure). Then there is a darker region corresponding to the first ZnCdMgSe layer, followed by the multi-QW structure. The second ZnCdMgSe and cap layer of ZnCdSe are seen on top. The first two wells of the multi-QW region exhibit diffuse interfaces, but the remaining 33 wells have sharp well-defined interfaces. No dislocations are seen in these low magnification images, indicative of coherent structures.

A higher magnification image of the multi-QW region is also shown in Fig. 5.1 (right side). Uniform ZnCdMgSe barriers layer thicknesses of 9.2 nm, and 3.4 nm for the ZnSe/CdSe layers were obtained. The contrast between the ZnSe/CdSe layers was not evident, and the layers could not be resolved individually. CdSe is known to produce quantum dots (QDs) when grown on ZnSe on GaAs substrates due to the large lattice mismatch when that substrate is used. The TEM images confirm that when grown on InP substrates and with strain compensation, good two-dimensional QW formation was achieved through the structure.

Fig. 5.2 shows the 2θ-ω scans for sample 2, which is representative of all the samples studied. For the measurement shown we aligned to the InP substrate (004) Bragg reflection. The
The main graph is plotted on a log-scale, and the scan was made over a wide range of $2\theta$ values (55.3-70.3). Many superlattice peaks are present in the scan, evidence of an excellent layered structure. The inset shows a linear scale plot over a narrow $2\theta$ range, close to the substrate peak. Based on the results of the calibration samples we could identify the ZnCdMgSe (shown), and ZnCdSe (not shown) 004 diffraction peaks.

Because of the highly strained nature of this system and to clearly identify the 0th order superlattice peak, we scanned the (004), (115), (113), (224) and (333) Bragg reflections and performed a graphical identification of the 0th order superlattice peak [84-86] for all the samples, and followed its evolution as the $t_{\text{CdSe}}/t_{\text{ZnSe}}$ was changed. From this we deduced the perpendicular lattice mismatch from the structures, which varied from -1.0% to +1.0%. The data are summarized in Table 1. The lowest mismatch was -0.23% for sample 3. Further adjustments...
of the relative thicknesses of the CdSe and ZnSe layers should result in a fully strain compensated structure with the desired mismatch value of less than 0.2% [28].

We investigated the intra-band optical transitions by performing PL measurements. Fig. 5.3 shows the room temperature cw-PL spectra of the samples. Bright PL emission was observed in the visible range, from the red (700 nm, 1.77 eV) to the orange (602 nm, 2.06 eV). The PL emission energy of all the multi-QW samples studied is below the bandgap of ZnCdSe lattice-matched to InP (Eg=2.1eV). This is a first indication that the system provides deeper QWs, and hence a larger CBO, by using strained CdSe layers as the well material. Single narrow peaks (FWHM 48-67meV) were obtained at room temperature for all the samples, and no deep level emission was present, indicative of high quality samples.

Room temperature FTIR absorption measurements gives us insight about the optical response due to ISB transitions in the infrared. The FTIR absorption spectra for the samples are shown in Fig. 5.4. Single peaks in the absorption are obtained as expected for symmetric QW structure due to the selection rules. Peak absorption was tailored from 3.83 µm (324 meV) in
Simulations of the conduction band energy levels in single symmetric step QWs were done to obtain the wavefunctions and discreet energy values expected for these structures. The 3.0 eV ZnCdMgSe barrier thickness of 9 nm is thick enough to prevent coupling in the QWs. In the simulations we vary the CdSe layer thickness from 9 ML to 3 ML, with integer ML values. The ZnSe total thickness was set such that the structure would be strain balanced, that is, the same number of MLs of ZnSe as MLs of CdSe. The QW structure was assumed to be symmetric, so that the ZnSe total thickness is distributed equally on each side of the CdSe layers (For example: 4.5 ML ZnSe/9 ML CdSe/4.5 ML ZnSe). The simulation parameters include the
effective mass of the electron in the conduction band of 0.11me, 0.15me, and 0.23me for CdSe (RT Eg = 1.7 eV), ZnSe (RT Eg = 2.7 eV), and MgSe (RT Eg = 3.6 eV), respectively, and a conduction band offset of 80% of the total band offset. From the simulation results, shown in Figure 5.5, only one electron bound state was obtained for 3 ML of CdSe, 2 bound states for 4-6 ML, and 3 bound states from 7-9 ML. We calculated e1-e2 transitions energies of 3.85 µm (322 meV) for 9 ML CdSe well, 3.43 µm (361 meV) for 8 ML, 3.04 µm (407 meV) for 7 ML, 2.68 µm (461 meV) for 6 ML, 2.39 µm (518 meV) for 5 ML, and 2.18 µm (569 meV) for 4 ML of CdSe. By comparing the simulation values with the measured absorption we could estimate the actual thickness of the CdSe layers to be ~9 ML for sample 1, 7 ML for sample 2, 6 ML for sample 3, and around 6-5 ML for samples 4 and 5.

Based on the simulation results we predict that we can reach wavelengths as low as 2.18 µm with the materials used here by reducing the CdSe (and corresponding ZnSe) thickness to 4 ML. Even shorter wavelengths can be obtained by increasing the barrier height using a higher MgSe fraction in the quaternary material. The binaries CdSe (as the well material) and MgSe (as the barrier) provide the maximum bandgap difference of the ZnCdMgSe alloy system, but if the strain between them and the InP substrate is not balanced it can lead to lattice relaxation and defects. An improvement of the structure quality is clearly evidenced by XRD scans when ZnSe
is used for strain compensation [87] as compared to when no strain compensation is used [88]. The incorporation of binary compounds in the active region of these structures may have other positive impacts on the material quality due to the absence of alloy disorder, which could result in more abrupt interfaces [89].

5.4 Conclusions

In this chapter we presented the MBE growth and characterization of strain balanced CdSe/ZnSe/ZnCdMgSe-based multi-QW structures grown on InP substrates. TEM, XRD and PL confirm the good structural and optical quality of the samples. PL also confirm the realization of red light emitters that are lattice matched to InP substrates. The ISB absorption of these multi-QW structures was observed at wavelengths as low as 2.56 μm, shorter than those possible with the commonly used InGaAs-based structures. Simulations based on these results predict that using a 3.0 eV ZnCdMgSe barrier wavelengths as short as 2.18 μm are possible with these strained compensated materials.
Chapter 6

Quantum cascade (QC) detectors

6.1 Introduction

Optical sensing of traces of molecular species is of great interest for many important applications [90]. Molecules exhibit absorptions in the IR, where their main vibrational and rotational signatures lie. To make these sensors, suitable light sources and detectors are needed. Quantum cascade (QC) lasers have become powerful and reliable current injection intersubband semiconductor sources of IR light [91], and similar technologies are being explored to produce detectors [21]. Development of integrated sources and detectors that operate at room temperature will be beneficial in the miniaturization of optical sensors [92, 93], reducing their energy requirements, and enabling their availability in commonly used wireless handheld devices. In this chapter we discuss the realization of these detectors.

QC detectors, like quantum well infrared photodetectors (QWIP) [94], are devices that rely on the intersubband transitions in quantum wells to detect IR light. QC detectors like the photovoltaic QWIPs [95,96], operate at no bias, which allows IR detection with less noise and eliminate the dark currents that are obtained in the conventional photoconductive QWIPs, and can operate up to room temperature. Both of these devices relies in an asymmetry in the conduction band to allow the movement of charge from a main quantum well. While PV-QWIPs relies on the use of several materials (3 or more) [96] and with modulation doping [95] to form that asymmetry. QC detectors are made with only 2 materials and create the asymmetry with a series of coupled quantum wells of a digitally graded superlattice forming a saw tooth bound
levels structure, similar to the ones of unbiased QC lasers. The use of an unbiased QC structure as a detector was first demonstrated by D. Hofstetter, et al. [97] where they used a QC laser structure as a detector. Since then the design and performance of QC detectors has improved. By considering no-bias operation in the detector design the exited energy from the active region is made degenerate with the bound state in the first extractor quantum well increasing the movement of the electron to it by resonant tunneling, where in a QC laser they are not aligned at zero bias, decreasing the escape probability (designed to align at the operating laser bias). The first QC detector made from a QC laser structure had a responsivity in the micro Amps/W range, and newer design got into the mili Amps/W range.

Thus far QC detectors have been made using only III-V semiconductors. QCDs made of GaAs/AlGaAs grown on GaAs substrates have targeted the 8[98], 8.8[99], 8.9[100], 12[101] and 84 μm[102], while those made from InGaAs/InAlAs on InP substrates are active in the 5.3[103], 8.0[104], 9.0[105], 10.7[106], and 19 μm[107]. Recently, GaN/AlGaN on sapphire substrates QC detectors have been reported covering the 1.55[108], 1.7[109, 110], 1.8[111], and 4.0 μm [112] wavelengths, while the QCDs made from InGaAs/AlAsSb on InP substrates QC detectors target the 2.1 and 2.5μm [113]. QC detectors made of InAs/AlAsSb on InAs substrates were active at 4.8μm [114], and InAs quantum dots QC detectors on InP substrates spiked their response at the 4.3[115], and 5.3μm [116]. While III-V materials work, many of they suffer from some issues, like low CBO that does not enable short wavelength operation (shortest GaAs/AlGaAs QCD wavelength is 8.0um, and shortest InGaAs/AlGaAs QCD wavelength is 5.0um), intervalley scattering becomes a limiting factor when strained materials are used, size non-uniformity in the case of quantum dots, not suitable substrates that make growth very
strained and internal fields that complicate design in the case of the nitrides, and InAs substrates are still very expensive.

When characterizing detector devices, three figures of merit are often used: the detection wavelength, the responsivity, and the detectivity. The detection wavelength is the specific wavelengths of light where a photocurrent is produced. The current responsivity, \( R \), is defined as the detector output current per unit of input power. This can be obtained by using a calibrated light source (usually a blackbody source, or a laser, and measuring the photocurrent produced by that known power. The detectivity \( (D^*) \) is the ratio between peak responsivity \( R_{\text{MAX}} \) and the mean noise current, then normalized by the detector area and the measured bandwidth.

In this chapter we will discuss the realization of the first II-VI material based QC detector. Then we will discuss our first approach towards making a broadband QC detector stacking 3 QC detection cores. Then we will discuss studies about two different arrangements of active cores (stacked or interleaved), to investigate which will help us reach broadband activity. We will end with the discussion of the realization of an interleaved 2 active cores broadband QC detector.

### 6.2 Realization of the first II-VI QC Detector

One main project we have been working in our laboratory is the realization of a II-VI material QC laser. The structure that resulted in our very first QC detector, and that we are about to describe, was designed to be a laser. In terms of growth, since they are current injected devices, the lasers were grown low n-type doped InP substrates (carrier concentration in the \( 3\times10^{17} \) range). Laser structures can generally be thicker than detector structures, since they require thicker layers to create an appropriate cavity to the optical fields inside the structure. In
our ZnCdMgSe-based lasers, they require 2 thick low-doped ZnCdSe waveguides layers, and 2 thick low-doped ZnCdMgSe cladding layers that sandwiched the active core, and all that is grown between the top and bottom contacts, which are made of highly doped ZnCdSe layers. All the following QC detector structures grown (and discussed later in this chapter) did not require cladding and waveguide layers, and the active cores were directly grown between the contact layers. Figure 6.1 shows an SEM images comparing a QC laser and a QC detector structure. The complete structure of this sample, from the InP substrate to the top (growth sequence) is as follows: 300nm InGaAs layer, 10nm of ZnCdSe low temperature buffer, 600nm of ZnCdMgSe as the bottom cladding, 850 nm of ZnCdSe as the bottom waveguide, the active core repeated 30 times for a complete thickness of 831 nm, a 300 nm ZnCdSe top waveguide layer, a 600 nm ZnCdMgSe top cladding layer, and a 400 nm heavily doped ZnCdSe layer as the
top contact. All the layers, besides the top contact layer, were chlorine doped to reach a carrier concentration of $3 \times 10^{17} \text{ cm}^{-3}$. The top contact was doped to reach a carrier concentration of $3 \times 10^{18} \text{ cm}^{-3}$.

This detector was originally designed to be a QC laser to emit at 4.8 $\mu$m. The structure design is a revised version similar to the laser structures designed and reported by Yu Yao [117]. The active core layered structure is given in Angstrom as: $10/26/9/30/8/36/20$ for the active region, and immediately following that, $15/16/16/14/17/12/18/10/20$ for the extractor region (where the ZnCdSe well layers are in bold, the ZnCdMgSe barrier layers are in italics, and the underlined ones are chlorine doped layers using the same ZnCl2 cell temperature as a calibration sample that yielded a carrier concentration of $3 \times 10^{17} \text{ cm}^{-3}$). The ZnCdMgSe alloy used for this device growth had a bandgap at room temperature of 3.0 eV, and it was closely lattice matched to InP substrate. This device was made with the highest magnesium content on the barrier, while

Figure 6.2: High resolution XRD $2\theta-\omega$ scan near the InP (002) Bragg reflection
all the other were designed and growth with a bandgap of 2.8 eV. Note also that this QC detector has a 3 well active region, and the extractor region is where the doping its placed, which later we change to a more conventional detector design of a one main doped quantum well as active region, and an undoped extractor region. The complete active core was repeated 30 times. This will create a superlattice in the structure that we will see in the XRD experiments. Adding all the layers thickness yields 27.7 nm, this is the designed length of the superlattice. The sample number of this first QC detector is A3307.

Figure 6.2 shows the HR-XRD scan around the InP (002) Bragg reflection. We can see many superlattice peaks that are indicative of good structural quality (sharp interfaces), and we can extract the length of the active core. The period calculations from the XRD measurements gave us a length of 27.0 nm, that is only 2.5% deviation from the design values, which indicate good control of the layer growth thicknesses. There was some compressive strain in the layers that made the SL(0) peak to appear on the left side of the substrate peak. The lattice mismatch from the SL(0) peak and the substrate is of 0.24%. This low number indicates good control over the lattice matching to the InP substrate.

Once we finished characterization of the grown detector structures, a piece of the sample was shipped to our collaborators in Princeton University. There the samples were processed into the detector devices. The samples were processed into rectangular mesas 310umx485um using standard lithographic and wet-etching techniques. The top and bottom metallic contacts were made of 25nm of Ti followed by 200nm of Au, deposited by e-beam evaporation. The top contact had a 300umx300um aperture to let the light in the sample from the top, and an additional 45o facet was polished in one of its side to shine the detector from there. The processed devices were mounted on a copper plate and inserted in a cryostat with optical
windows for temperature dependent measurements. This processing of the samples into devices done at Princeton applies to all the detector devices discussed in this chapter.

In figure 6.3 we show the photoresponse of the QC detector device as a function of temperature and at zero applied bias. The photocurrent was measured sending the IR light of the FTIR glowbar through the 45° polished facet, as shown in the figure inset. The glowbar IR light was pass through a chopper and the current measurements were done using lock-in amplifier techniques. We can notice a combination of three peaks in the spectra. One sharp intense peak is centered at 2826 cm\(^{-1}\) (3.5 μm, 350 meV) and then two peaks join to make a broader less intensity feature centered at 3672 cm\(^{-1}\) (2.7 μm, 455 meV) and 4135 cm\(^{-1}\) (2.4 μm, 512 meV).

To be able to identify and explain why we get these peaks from the structure we rely on simulations on the conduction band structure of the structure at no-bias. Results of this specific simulation are shown in figure 6.4. There the most relevant energy levels are labeled.
The main transition E1-E3 has a value of 301 meV (4.1μm), while the other two transitions in the active region are E1-E4 and E1-E5 with transitions energies of 417 meV (2.97μm) and 530 meV (2.33 μm), respectively. As we can see the simulated energies are slightly lower than the detected energies. This is due to the fact of the growth reduction on the thicknesses from the design. As we described before with the measurements of the XRD period, the whole structure is 2.5% smaller than the design. If we consider that the error is only in the well material, to match the grown structure the design must be 1 Å less in each well. When this is considered in the simulations, the calculated theoretical transitions E1-E3, E1-E4, and E1-E5 become 352meV (3.52 μm), 456meV (2.71 μm), and 560meV (2.21 μm), respectively, close to the observed values.

The intensities of the peaks can be explained by the fact that E3 is closer to the extractors energy levels, this make that tunneling more probable, also the propability of the intersubband
transition, defined as the overlap integral of the lower energy wavefunction with the derivative of the exited wavefunction decreases for the E1-E4, and E1-E5 transitions.

The three figures of merit for our first QC detector are: operating wavelength at 3.5 μm (disregarding the lower intensity, shorter wavelength activity), current responsivity $R = 0.1$ mA/W, and detectivity $D^* = 2.5 \times 10^{10}$ Jones. The low current responsivities that we obtained are associated to the fact that this structure was designed to be a laser. As we can see in the simulations of the conduction band, the exited levels in the active region are not near degeneracy with the first extractor energy level. This will reduce the tunneling probability of the charges moving thru the structure and therefore its low responsivity. In later designs we fixed this by using a more conventional QC detector design where the electronic energy levels of the main QW exited state and the first bound state in the adjacent extractor QW are nearly degenerate to increase the tunneling probability from the active region and the extractor. More information about this detector can be found on Ref. 76.

6.3 First attempt towards a Broadband QC detector: Stacking of 3 QC detector cores

A desired advantage in IR detectors is multicolor or broadband functionality. It is a property that is sought in recent development of commercial arrays [118]. For scientific applications, such as spectroscopy, broadband IR detection is required. The spectral activity of a detector is a limiting factor in spectroscopic systems. Imaging systems benefits from a broadband detector, where the activity in different spectral ranges can be obtained from the same device by the application of different filters. After realizing the first single core II-VI QC detector from a QC laser structure we were convinced that we could enhance the responsivity of our devices by addressing the design. Now we wanted to focus on making a detector that work
on several wavelengths. To make a detector with a broadband response. Even though narrow band detectors are useful on the detection and selectivity of certain species, commercial application of IR detectors, like the ones used in FTIR spectroscopy made of mercury-cadmium-telluride (MCT), etc. has a broadband response. The advantage of intersubband detectors to work up to room temperature make them attractive to realize them for the first time. Here we will report the realization of broadband detection by combining several QC cores.

There are several examples in the literature of combining more than one active core to make a broadband detector. In their paper, D. Hofstetter, etal. [119], stacks 6 types of active cores on top of each other by repeating each one three or five times each. They achieved broadband detection with a response from 4.7 to 6.8 μm (ΔE/E=27.3%), and responsivity of 13 mA/W at the very low temperatures of 10K. We tried this approach of stacking detector cores, but with many more repeats. We designed 3 different QC detectors cores that their center wavelength were designed to be 5.5 μm, 6.8 μm, and 8.0 μm. By combining these three cores we expected to have a detector with a response from 4-9 μm. The design of these QC detectors relied in a more conventional design, where there is only one main QW doped as the active region, and then a series of coupled QWs form the extractor region.

For the 8.0 μm detector core, the active region layers were 14/54/24, and the extractor region grown immediately after that were 19/24/20/14/23/12/29/12/39. For the 6.8 μm detector core, the active region layers were 14/50/24, and the extractor region were 17/24/18/14/23/12/23/12/30/12/37. For the 5.5 μm detector core, the active region layers were 14/42/24, and the extractor region were 13/24/14/18/12/21/12/26/12/31. Again, for all these descriptions the ZnCdSe well layers are in bold, the ZnCdMgSe barrier layers are in italics, and the underlined ones are chlorine doped layers. These time we raised the doping concentration in
the structure and for doping the main QWs we used the same ZnCl$_2$ cell temperature as a calibration sample that yielded a carrier concentration of $1 \times 10^{18}$ cm$^{-3}$. The period of the 8.0, 6.8 and 5.5 μm cores are 28.4, 31.0 and 27.7 nm, respectively.

The device structure did not have thick ZnCdSe waveguide, and thick ZnCdMgSe cladding layers after the bottom contact and before the top contact like our first detector. It was also grown on semi-insulating (S.I.) InP substrates, besides a low doped n-type substrates used before, this may be an advantage in the growing perspective because all our calibrations samples are grown on S.I. substrates, and I believe the quality of the S.I. substrates is better compared to the doped ones (even though more experiments need to be done to corroborate this). The complete structure of the sample given in order of growth from the substrate is the following: 130 nm InGaAs buffer layer, 10 nm of low temperature ZnCdSe, 800 nm of a bottom contact of ZnCdSe chlorine doped up to a carrier concentration of $3.0 \times 10^{18}$ cm$^{-3}$, then the 8.0 μm detection

![A3444 HR-XRD (004)](image)

Figure 6.5: HR-XRD of 3 core stacked QC detector.
core, repeated 15 times, followed by the 6.8 μm detection core, repeated 15 times, then the 5.5 μm detection core, repeated also 15 times, ending with a 400nm top contact of ZnCdSe chlorine doped up to a carrier concentration of 3.0x10^{18} cm^{-3}. The sample number of this detector is A3444.

Figure 6.5 shows the HR-XRD scan of the stacked 3 core detector sample around the InP (004) Bragg reflection. As we can see from this scan, this particular sample suffered from a relatively big lattice mismatch between the ZnCdSe layers and the substrate. This is evident by the modulation of the superlattice peaks intensity, where we see them of higher intensity in the left side, than in the right side of the substrate peak. Since the structure has thick ZnCdSe bottom and top contacts, we could see the contribution of that layer in the XRD spectra and calculate the mismatch. It turns out that the layer with the substrate was 0.62% mismatch. Even though this big mismatch might affect the quality of the structure, the sample grew with streaky 2x1 RHEED patterns through the end of growth and devices could been made out of it. Multiple superlattice peaks can be observed. By the nature of the structure (several different periods repeated) it is very difficult to identify and measure the period of each core.
Sample was shipped to Princeton and detector devices were made and characterized. The photoresponse of this sample is shown in Figure 6.6. As we can see a single sharp peak centered at 5.5 μm is obtained. There is some activity on the lower energy side, but it’s below the 15% of the maximum responsivity. This results indicate like if only one of the cores, the very top one of 5.5 μm, was active, and the remaining two where mostly inactive. In terms of responsivity of the device, we saw an improvement, due to improvements in the design, but the detectivity of this device was lower, due to more noise in the device. The greater noise maybe due to the high mismatch and the generation of electron escape paths thru defects in the structure. In conclusion, the three figures of merit for our second QC detector are: operating wavelength at 5.5 μm (disregarding the lower intensity, longer wavelength activity), current responsivity R= 3.5 mA/W at 80K, and detectivity D* = 6.0x10^8 Jones.

6.4 Investigation of different arrangements of QC detector cores towards broadband activity

Trying to understand the results of our last QC detector where the stacking of large repetitions of 3 cores only yielded activity of the core closest to the top contact, we retake the realization of a broadband QC detector by examining different approach on the growth arrangement of the cores. We step back from the number of cores, and this time used only two detecting cores. These two new cores are designed to be centered at 4.8μm and at 5.8μm. We grew several samples with different types of arrangements, a new interleaved design, and also a stacked one, and compare their results. The two detection cores, were designed [120] and grown as follows. First is the main quantum well, where absorption takes place, was doped with chlorine. The operating wavelength is designed there by a vertical transition between the first
two bound states in that well. The following two adjacent QWs are grown to have their allowed single bound energy state almost degenerate with the first exited energy state in the main quantum well. After that, a series of coupled quantum wells (5 QWs for the 5.1μm core, and 4 QWs for the 5.9μm one) were grown to complete each core, with thickness such that the energy difference from the first bound state from one QW to the next one of 35 meV. With this design, phonon assisted diagonal transitions are responsible to extract the electron towards the next core, where absorption can occur again, etc. The total design thickness of each core was 38.0nm for the shorter wavelength one, and 36.7nm for the longer wavelength one. For the long wavelength (5.8μm) core, the active region layers were 28/44/28, and the extractor layers were 14/28/14/30/17/26/21/28/26/30/33. For the shorter wavelength (4.8 μm) core, the active region layers were 28/38/28, and the extractor layers were 11/28/11/28/13/30/16/26/19/28/23/24/29.

The ZnCdSe well layers are in bold, the ZnCdMgSe barrier layers are in italics, and the underlined ones are chlorine doped layers. The doping concentration in the structure and for doping the main QWs we used the same ZnCl₂ cell temperature as a calibration sample that yielded a carrier concentration of $1 \times 10^{18}$ cm⁻³. The period of the 5.8 and 4.8 μm cores are 28.4
and 27.7 nm, respectively. Figure 6.7 shows the results on the quantum mechanical simulations done on those structures. The sample numbers for these QC detectors with 2 cores are A3655 and A3657, using the interleaved design, and A3669 done with the stacked design.

We investigated two different designs that we will call the “interleaved design” and the “stacked design”. Figure 6.8 show a diagram of both sample arrangements. In the interleaved approach we grew one core designed for one wavelength, followed by the core designed for the second wavelength. The sequence of the two cores was repeated 30 times and sandwiched between two ZnCdSe layers doped n-type by chlorine. In the stacked design we first grew 30 repetitions of the longer wavelength core, and then on top of this we grew 30 repetitions of the shorter wavelength core. Then the stack of two cores was sandwiched between two ZnCdSe doped layers. These doped ZnCdSe layers will become the top and bottom contact layers that will be used in the device fabrication. The thickness of the top contact was of 100nm, and the
thickness of the bottom contact was 800nm. The bottom contact was grown thicker to facilitate access of this layer via wet etching.

After growth the samples were characterized by high resolution X-ray diffraction (XRD), field emission scanning electron microscope (SEM), and FTIR transmittance experiments. All the post grown characterization was done at room temperature. XRD experiments were performed with a Bruker D8 discover set up, with an analyzer crystal before the detector for high resolution. SEM was performed with a Field Emission source Zeiss Supra 55 VP setup. The samples were cleaved right before inserting them in the microscope to obtain images of the transverse cut. For the IR transmittance experiments, the samples were polished making 45° facets to create a multi-pass geometry. The light from a Nicolet Nexus-870 FTIR interferometer was passed through a wire linear polarizer, focused to pass through the sample, and collected with a nitrogen cooled MCT detector.
SEM images of the transverse cut of the interleaved and stacked QC detector structures are shown in figure 6.9. The images show similar overall structures, since the repeats for each of the cores for the two designs were chosen so that the two designs had the same thickness. The SEM showed modulations, dark and bright fringes in active region of the detector were the cores are due to the contrast between the barrier (ZnCdMgSe) and well (ZnCdSe) materials that make up the core regions.

High resolution XRD 2θ-ω scans near the InP (002) Bragg reflection are shown in figure 6.10. Both scan show many superlattice peaks indicative of the samples good structural quality. The interleaved QC detector scan shows more superlattice peaks in the same angular range than the scan stacked QC detector, indicative of a bigger superlattice period in the interleaved sample than in the stacked one. An average period from the contribution of each superlattice peak was calculated and we obtain an XRD measured period of 71.6nm for the Interleaved and 37.1nm for the stacked sample. This values are very close to the design values of 74.7nm (sum of the length
of both cores) for the interleave sample and 37.3nm (average of the total length of both cores) for the stacked one.

The spectral response of each structure was measured via IR transmittance experiments. The IR absorption results are shown in figure 6.11. The absorption of the stacked sample shows a single sharp peak at 2100 cm\(^{-1}\) (4.8\(\mu\)m). This absorption peak overlaps with the short wavelength core design, which was grown closer to the top contact. As in the 3 core stacked detector previously described, only the top stack of cores is active. Broadband response is achieved, but only of low intensity (below 65\% of the maximum absorption). A sample grown with interleaved design was also measured in IR transmittance. It show maximum peaks at the lower energy side at 1697 cm\(^{-1}\) (5.9 \(\mu\)m), the absorption then decreases a little in the high energy side. FWHM of each sample absorption was 835cm\(^{-1}\) for the stacked sample, and 860 for the
interleaved one. Even though at the half-maximum there is a broader response of the interleaved, this becomes even more evident when we measure the full width at 70% of the maximum, which yields 359 cm$^{-1}$ for the stacked sample, and 638 cm$^{-1}$ for the interleaved one. With this results we show that the interleaved arrangement of the cores is more suitable to achieve broadband detection.

The reason for only showing the top stacked core working in the stacked design QCDs could be because of the electric field distribution inside the sample. Boundary conditions for the electric field on the semiconductor/highly doped contact region near the top of the sample require the electric field to be maximum at this boundary. Since the field is stronger in the top, the core grown closest to the top contact interacts more with the stronger field, and therefore is the most active one in the stacked arrangement. Since the interleaved design have the cores sequentially grown, both cores take advantage of the field maximum areas. The growth of QCDs placing longer wavelengths stack on top could verify this.

The stacking of several active cores has been proven to work to produce broadband emission in QC lasers [121-125]. We tried this approach twice in detectors and their spectral response were not broad. This does not disregard the stacking of cores as a viable way to achieve broadband detection, but if used, careful positioning of the cores must be considered throughout the structure to take advantage of the different field distributions by different wavelengths, or by using shorter periods of stacks, like in Ref. 30. Here we have tried the shortest period of stacking, one right next to the other, calling it an interleaved design, and have obtained activity of all the cores used in the device, leading to broadband activity. To our knowledge this is the first time that this interleaved arrangement of cores has been tried in an
intersubband device. We conclude that the interleaved design used in QCDs provide an easy arrangement of cores that yield broadband activity.

**6.5 Realization of a broadband QC detector with 2 cores interleaved**

![Figure 6.12: a) Photoresponse of Interleaved sample b) temperature dependent photoresponse of interleaved sample.](image)

From the interleaved wafer we were able to make devices. In depth results of the characterization of these devices has been published elsewhere [120]. We are just going to highlight here some of the device results. We obtained a broad and smooth spectral response between 3.3-6.0μm. The cores were centered around 5 and 6 μm, so we expected a broadband response from 4-7 μm, but the reduction in the structure thickness measured by the XRD period calculation, and the fact that the barriers where 100meV higher than design (measured by photoluminescence in a bulk ZnCdMgSe sample, not shown), both effects combined results in a blue shift of the detection wavelength to the observed 3.3-6μm. We obtained peak responsivity of 40mA/W @ 80K, and response was measured up to room temperature. The detectivity was 3.1x10^{10} Jones, and with only two cores we were able to achieve a spectral width over 1000cm⁻¹.
Figure 6.12(a) shows its photoresponse at 80K, and (b) its photoresponse as a function of temperature.

6.6 Conclusions

In this chapter we have shown the results of the several ZnCdMgSe-based QC detectors. Table 6.1 shows the figures of merit of these detectors. We started with the realization of the first II-VI QC detector from a QC laser structure. After that our focus was to make a broadband QC detector by combining several cores. Our first attempt with a 3 core QC detector with 15 repetition stacked one on top of the other did not achieved a broadband detection. This lead us to investigate two types of core arrangements, the interleaved design, where a core is grown right next to the other different one, and the staked arrangement where a the same core is repeated several times first grown and the other type of core is grown above that. By FTIR absorption the stacked sample shows a sharp peak, while the interleaved arrangement show broader absorption, which led to the conclusion that this type of core arrangement is more suitable to produce broadband QC detectors. We ended the chapter with the results of the realization of a broadband II-VI QC detector based on the interleaved design.

Table 6.1: Figures of merit of the QC detectors discussed in this chapter.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Type of detector</th>
<th>Peak wavelength</th>
<th>Responsivity</th>
<th>Detectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>A3307</td>
<td>QC laser, single core</td>
<td>3.5 μm</td>
<td>0.1 mA/W</td>
<td>2.5x10^10 Jones</td>
</tr>
<tr>
<td>A3444</td>
<td>3 cores stacked</td>
<td>5.5 μm</td>
<td>3.5 mA/W</td>
<td>6.0x10^8 Jones</td>
</tr>
<tr>
<td>A3655</td>
<td>2 cores interleaved</td>
<td>4.4 μm</td>
<td>40.0 mA/W</td>
<td>3.1x10^10 Jones</td>
</tr>
</tbody>
</table>
ZnCdMgSe-based Semiconductor Disk Lasers for green emission

7.1 Background and motivation

In the previous chapters we have discussed devices that rely on intersubband transitions happening within the conduction band. The energy scale of these transitions are in the meV range or micro-meter wavelength range. Here we will describe a device that relies on intraband (or band to band) transitions in structures made with intrinsic (undoped) semiconductors. The energy scale of these transitions are in the several eV range or nano-meter wavelength range.

Semiconductor lasers are widely used as compact coherent light sources in a multitude of applications that impact the fields of medicine, spectroscopy, communications, data storage, and compact displays. However there is a paucity of robust semiconductor lasers operating in the 500 - 630 nm spectral range, which is important for these applications [126]. To fill this ‘visible gap’ several semiconductor material systems are being investigated, including the group III-Nitrides [127], and low-dimensional structures such as quantum wire [128] and quantum dot systems [129]. Another material system able to address this gap is the II-VI Zn$_x$Cd$_y$Mg$_{1-x,y}$Se family of semiconductors lattice-matched to InP. This family of materials enables direct bandgap tunability from 2.1 eV to 3.6 eV, and thus provides an attractive route to heterostructures with emission at visible wavelengths. Current-injection edge-emitting lasers based on II-VI semiconductor materials have been demonstrated [130, 131]. However, those II-VI bi-polar electrically-driven devices suffer from short operating lifetimes due to difficulties with p-type doping in most wide bandgap semiconductors. To avoid these p-doping issues, we decide to
pursue optically-pumped II-VI based semiconductor based lasers. There have been several reports on optically-pumped vertical-emitters and vertical cavity surface emitting lasers (VCSELs) based on II-VI semiconductor quantum wells (QWs), quantum-dots (QDs), coupled QD-QW systems as active materials and novel micro-cavity design [132-142]. The materials systems investigated include ZnSe-based quantum structures, ZnSSe and MgS/ZnCdSe superlattices, and combination of III-nitride and II-VI materials, such as, GaN-ZnSe. These II-VI semiconductor quantum structures and micro-cavity designs have led to the demonstration of laser action in the green and blue-green spectral regions.

Here we are pursuing Zn$_x$Cd$_y$Mg$_{1-x-y}$Se-based alloys of different compositions grown on InP substrates to fabricate fully lattice-matched optically pumped emitters. Our group has already demonstrated Zn$_x$Cd$_y$Mg$_{1-x-y}$Se-based optically-pumped edge-emitting lasers in the red-green-blue (R-G-B) region [7], and distributed Bragg reflectors (DBRs) [143] working in the visible range. These materials have a large range of compositions that can be grown lattice-matched to InP, which is the substrate of choice. The family of lattice-matched materials can be combined in complex multi-layered structures without the presence of strain, thus eliminating strain induced structural degradation [144]. Here we combine edge emitters and DBR structures with the goal of demonstrating an optically-pumped semiconductor disk laser (SDL) operating in the green spectral region.

Optically-pumped SDLs based on III-V semiconductor materials are now well-established, both in research and industry, with fundamental emission covering most of the spectral region from the visible red to the mid-infrared [145, 146]. SDLs with fundamental laser emission in the applications-rich violet-to-blue range have been targeted with InGaN on GaN.
and II-VI on GaAs-based structures [142], with limited success; however, green-yellow-orange emission is a challenge for these materials.

In this chapter we will discuss three structures based on Zn$_x$Cd$_y$Mg$_{1-x-y}$Se materials grown on InP substrates with an InGaAs buffer layer by MBE: two multiquantum well (MQW) gain structures and a DBR structure. One of the MQW gain structure was directly grown on an InGaAs/InP substrate; and the other on a 5-period DBR structure to isolate it from the substrate. These MQW structures were designed for anticipated room-temperature SDL operation around 540 nm. In both cases the MQWs were contained within wider bandgap Zn$_x$Cd$_y$Mg$_{1-x-y}$Se pump-absorbing barrier layers, forming a double heterostructure geometry. The 5-period DBR on which the second gain structure was grown, was also grown on InGaAs/InP substrates. The third sample, the 20-period DBR structure, was grown to investigate the reflectivity of these materials to fabricate DBRs. We used X-Ray diffraction (XRD) and scanning electron microscopy (SEM) to study the structural quality of the samples. Their spectroscopic properties were investigated using steady-state and time-resolved surface photoluminescence (PL) measurements. Reflectivity measurements were carried out on the DBR samples. Edge emission from cleaved cavities of these materials was also investigated. Our results suggest that these materials are promising for the fabrication of SDL devices operating in the green-yellow wavelength region.

7.2 Design, growth and characterization of ZnCdMgSe-based Semiconductor Disk Lasers

The samples under study were grown in a dual-chamber MBE system as described in chapter 2. The substrate of choice for all the samples was semi-insulating InP (001). The composition of all the constituent materials needed for each sample was calibrated so they would be closely lattice-matched to the substrate; specifically the lattice-matched Zn$_{0.47}$Cd$_{0.53}$Se alloy
Three different Zn\textsubscript{x}Cd\textsubscript{1-x}Mg\textsubscript{1-y}Se alloy compositions were needed for the three samples. The Zn\textsubscript{0.47}Cd\textsubscript{0.53}Se-based QWs were designed for room temperature green light emission at around 540 nm. Samples with single QWs were grown to calibrate this emission.

Schematic diagrams of the layer structures of the samples investigated are shown in Fig. 7.1. The first is a MQW double heterostructure grown directly on the substrate/InGaAs buffer, which will be called Sample A (Fig. 7.1(a)). The MQW region was designed for resonant periodic gain (RPG) [149] at the design wavelength of 540 nm. A similar MQW structure was grown on top of a 5-period DBR, which will be called Sample B (Fig. 7.1(b)). The 5-period DBR was added to set the sub-cavity resonance of the structure; the reflectivity is not sufficient for a SDL end mirror. A 20-period DBR structure designed to operate in the green region was also grown (Fig. 7.1(c)). Samples A and B contain nine quantum wells of Zn\textsubscript{0.47}Cd\textsubscript{0.53}Se alloy
embedded in a 2.7 eV bandgap Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-x-y}Se barrier material, all of which is sandwiched between two higher bandgap (3.0 eV) Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-x-y}Se transparent carrier confinement layers. The 5-period DBR of sample B and the 20-period DBR structure consist of alternating Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-x-y}Se layers with compositions corresponding to a 2.5 eV and a 3.0 eV bandgap. The bandgaps were chosen to maximize the refractive index step between the two layers while maintaining high quality growth, without introducing absorption in the green. The actual alloy composition values are given in the Results and Discussion section below. Since many of the constituent materials contain Mg, every structure is capped with a 10-nm layer of Zn\textsubscript{x}Cd\textsubscript{1-x}Se, to avoid oxidation.

The structural quality of the samples was examined by high-resolution XRD and SEM. To investigate the optical spectroscopic properties of the structures we carried out steady-state PL, reflectance, intensity-dependent PL, and time-resolved PL measurements.

7.3 Results and discussions
Fig. 7.2 shows the XRD 2θ-ω scans near the InP (004) reflection for the three samples under study. All the scans exhibited thickness fringes from the InGaAs layer that can be clearly seen when plotted on a log-scale (shown in the inset of Fig. 7.2(a)). These are indicative of a good quality InGaAs layer, with a good III-V to II-VI interface. The good surface quality of the InGaAs buffer was also confirmed by the observation of sharp and streaky RHEED patterns with an As-stabilized (2x4) reconstruction (not shown). From the XRD fringes we calculated the InGaAs buffer layer to be 225 nm thick, which matches well with its SEM measured thickness.

In the XRD spectrum of Sample A, displayed in Fig. 7.2(a), there are three weak peaks close to the InP (004) peak, corresponding to the three thicker layers making up the structure. From the position of the peaks we estimate that the greatest lattice mismatch of any of the layers in the structure is $|\Delta a/a| \sim 0.22\%$. The XRD spectrum of Sample B, presented in Fig. 7.2(b), shows three sharp peaks assigned to the DBR superlattice reflections (marked with arrows), as well as other peaks corresponding to the various other layers. We conclude that the greatest lattice mismatch of any layer in the structure is $|\Delta a/a| \sim 0.14\%$, as indicated by the proximity of the peaks to the InP peak. The corresponding spectrum of the 20-period DBR sample (Fig. 7.2(c)) shows several peaks which we attribute to the InGaAs and the superlattice satellite peaks.
The inset of Fig. 7.2(c) shows the (002) scan, which was taken to help identify the 0th order superlattice peak. In this case, the lattice mismatch of the structure is less than $|\Delta a/a| = 0.20\%$.

From the superlattice satellite peaks we can estimate the period of the DBR structures. For sample B, the calculated thickness of the DBR period from the XRD data was 119 nm and for the 20 period DBR sample, the XRD calculated period was 120 nm, both less than 10\% larger than the design thickness (109 nm).

The cross sectional SEM images of sample B and of the DBR sample are shown in Fig. 7.3(a) and 7.3(b), respectively. All the layers in the structure of the samples could be resolved using the field emission SEM. The layer thicknesses were consistent with the design values to within a thickness error of less than +10\%. The darker regions in all the images correspond to the largest bandgap material, the 3.0 eV $\text{Zn}_x\text{Cd}_y\text{Mg}_{1-x-y}\text{Se}$, and the lighter grey areas are of the lower bandgap materials. For sample B the DBR period was measured to be 119 nm, in excellent agreement with the value obtained by XRD. For the DBR sample, the SEM image gives a period of 116 nm, also in good agreement with the XRD value. From the SEM and XRD studies we conclude that good structural properties and close agreement with the design values were obtained.
To explore the optical properties of the structures, steady-state PL spectra were measured along the normal to the sample surface for each sample at 77K, and the results are shown in Fig. 7.4. The spectrum of each sample is dominated by a sharp excitonic QW peak, and several higher energy peaks. Each peak in the spectra could be assigned to optical transitions originating from the different constituent materials in the structure. As expected, the intensity of the highest energy transition ~ 400 nm (barrier layer) is very weak compared to the QW ground state excitonic transition, but it could be resolved when the spectral region was magnified, as shown in the figure.

The PL spectrum of sample A, displayed in Fig. 7.4(a) shows three peaks at 537 nm, 461 nm, and 403 nm, which correspond to e1-h1 transition in the QWs, the band to band transitions in the Zn0.37Cd0.33Mg0.30Se pump absorbing barrier material, and the wide bandgap Zn0.25Cd0.19Mg0.56Se carrier confinement layers, respectively. The Sample B spectrum (Fig. 4(b)) shows four peaks at 523 nm, 490 nm, 457 nm, and 409 nm, corresponding to the e1-h1 transition in the QW, the low bandgap Zn0.42Cd0.38Mg0.20Se component of the DBR, the mid-bandgap Zn0.37Cd0.32Mg0.31Se pump absorbing barrier layers, the wide bandgap Zn0.27Cd0.20Mg0.53Se confinement layers, respectively. The 20-period DBR structure spectrum (Fig. 4(c)) is dominated by the emission of the low bandgap energy Zn0.42Cd0.38Mg0.20Se layers at 488 nm. The highest bandgap Zn0.24Cd0.17Mg0.59Se layers at 396 nm can also be seen. These
values of composition are the actual compositions grown, calculated based on the measured bandgaps and lattice constants. The measured emission wavelength values are compared with the design values for the structure in Table 7.1. An error of 5% or less between the desired value and the measured value is observed throughout.

Fig. 7.5 shows the reflectance spectrum for the 20-period DBR sample. A dip in the reflectance spectrum at ~600 nm is attributed to the absorption effects of the top ZnCdSe cap layer (Eg=2.1 eV, 600 nm). An 84.2% maximum reflectance, centered at 559 nm, was obtained. The figure also shows the simulated reflectance spectrum for a 20 period DBR assuming a Δn of 0.285. The close agreement between the stop-band width of the simulated spectrum and the measured spectrum confirms that there is a good estimate of the index step (Δn) in the simulation. The lower maximum reflectance of the grown structure is likely due to absorption in the buffer layer and cap layer, which could be included in the model. Using this value of Δn, we estimate that approximately 40 periods must be grown in order to obtain a 99.9% reflecting
dielectric mirror, as needed for the SDL structure. It should be noted that since the layers are lattice-matched to the substrate, a 40-period DBR structure can be realized with this material system without degradation of the structural quality. Although a larger number of periods are needed to achieve 99.9% reflectivity from the DBRs presented here compared to other II-VI

Figure 7.6: (a) Room temperature PL spectra measured along the normal to the sample surface at different pump powers for sample A. (b) Plot of PL intensity vs pump power measured at the two PL peaks, 547 nm and 568 nm. To avoid overcrowding representative (not all) spectra recorded at pump powers above and below the threshold are shown in (a).

Figure 7.7: (a) PL spectra measured along the normal to the sample surface at different pump powers for sample B. (b) Plot of PL intensity vs pump power measured at the two PL peaks, 539 nm and 548 nm. To avoid overcrowding representative (not all) spectra recorded at pump powers above and below the threshold are shown in (a).
Based DBRs reported in the literature, [150-152] our structures are better suited for emitters operating in the green wavelength range.

To further investigate the optical spectroscopic characteristics of these structures we carried out intensity dependent measurements of the PL spectra of samples A and B at room temperature. The results for sample A are shown in Fig. 7.6(a) and 7.6(b), and those for sample B are shown in Fig. 7.7(a) and 7.7(b). The surface PL is modulated by sub-cavity resonances, caused by the etalon effect between the semiconductor/air interface and the InGaAs/DBR, indicated by the double peaks around the QW emission with a separation of about 20 nm. For sample A, the strongest peak of the PL spectrum is at 547 nm for pump powers below 8 mW. At higher pump powers the PL emission at 568 nm becomes more prominent. This lower-energy emission dominates the spectrum at higher pump powers, and increases with pump intensity at a faster rate than the observed increase with intensity at low powers. This can be clearly seen in Fig. 7.6(b) from the abrupt increase in the slope of the 568 nm luminescence, while the PL at 547 nm becomes sub-linear. The spectra of Sample B, shown in Fig. 7(a), exhibits a qualitatively similar behavior. In that case, for pump powers below 3 mW the main PL peak emission is at 539 nm, while above 3 mW, the PL emission at 548 nm dominates. The PL intensity at 548 nm increases at a much faster rate (higher slope) with pump intensity (Fig. 7.7(b)) above 3 mW, while the luminescence at 539 nm continues at a sub-linear rate throughout. The change in the slope of the PL intensity with pump power may be indicative of the onset of amplified spontaneous emission (ASE) or of stimulated emission; however, we have not decoupled the influence of an improving overlap between the QW PL and a sub-cavity resonance with increasing pump power (and thus increasing temperature).
Room temperature time-resolved PL measurements at different excitation intensities were also carried out to further investigate the intensity dependence of PL. The measurements made at low and high pumping intensities for samples A and B are shown in Fig. 7.8. In each case we show the lifetimes of the PL at the two peak wavelengths. The time evolution of the PL of sample A at the two wavelengths for pump power of 7.5 mW is presented in Fig. 7.8(a). PL decay times were measured to be 386 ps and 319 ps at 547 nm and at 568 nm, respectively. When pumping sample A with pump power of 9.5 mW, the PL decay times were 417 ps and 75 ps at 547 nm and 568 nm, respectively, as shown in Fig. 8(b). Thus, at higher pump powers the lifetime of the 568 nm PL peak is greatly reduced, while that of the 547 nm PL peak remains the same within the experimental-uncertainty range. The shorter lifetimes are consistent with an ASE mechanism, while the longer lifetimes are indicative of spontaneous emissions. Similarly, when sample B was pumped at 0.8 mW, the decay times of the PL at 539 nm and 548 nm wavelengths were 1070 ps and 616 ps, respectively, as shown in Figure 8(c). With 3.0 mW
pump power the decay times were 1106 ps and 129 ps, respectively, as shown in Figure 7.8(d). Again, the spontaneous emission lifetime remains comparable, but the onset of ASE at 548 nm is accompanied by almost a factor-of-5 reduction in lifetime. It should be noted that the lifetimes of luminescence from sample B (with a DBR) were found to be longer than those in sample A (without DBR). This feature may be attributed to increased photon lifetime due to stronger field enhancement of the sub-cavity caused by the DBR. It will be instructive to carry out a rate-equation analysis of the time-resolved PL data to extract spontaneous emission rate and its enhancement (through Purcell effect) by the micro-cavity. We plan to pursue this when the cavity design is further improved to support laser action.

7.4 Epitaxial lift off of the SDLs and their applications to optical communications

Here we will give a brief summary of additional work done with our collaborators at the UK with samples grown with the same design as sample B discussed above. Once the samples were grown and characterized by us, we sent them to the University of Strathclyde, UK for processing and further characterization. Since these SDLs did not have a full DBR on them, the substrate will end up absorbing most of the light emitted by the QWs. In order to use them as gain structures in an external cavity system, the substrate had to be removed. Applications as color converters were also pursued.

To remove the substrate the sample is bonded to a glass slide using poly-ethylene glycol (a water soluble wax). The substrate is polished down to ~100um with sandpaper, then the InP is removed complete using a HCl:H3PO4 (3:1). The InGaAs layer serves as an etch stop, so the sample can be left in this solution without having to watch it constantly. To remove the InGaAs we use a solution composed of H3PO4:H2O2:H2O (1:1:6). Unfortunately, this solution also
etches the II-VI layer somewhat, but the etch rate of the InGaAs is much faster than that of the II-VI layer (18:1). A good knowledge of the InGaAs thickness, and the solution etch rates are necessary for this step. After this, the II-VI structure remains bonded to a glass slide and wax, which are inserted in hot water. The semiconductor layer membrane then floats in water, and it can be bonded to other substrates. Sapphire, glass and diamond substrates were used.

Photoluminescence studies were performed before the removal of the InP substrate, and after the bonding to the new substrate, to show that the optical quality of these layers are conserved. The PL did not change for the samples, demonstrating that the procedure does not harm the materials.
The benefits of heat spreading from bonding the membranes into diamond were observed when comparing the photoluminescence of the sample as a function of the pumping power of the laser source (Shown in figure #7.9). No shift of the photoluminescence was observed as the pumping power was increased. On the other hand, the one bonded to glass redshift the photoluminescence as the pumping power is increased, indicating that the heat from the pumping laser is not dissipated as well as diamond. For this procedure of substrate removal and exchange...
to work, the lattice mismatch of the MBE grown structure with the substrate has to be kept very low. Samples with a larger lattice mismatch than 0.4% resulted in cracking when the substrate was removed.

Taking advantage of the ability of producing these gain membranes, one application tested was its usefulness for optical communications using visible light. Here the membranes can be used as color converters, and with the same pumping laser, produce different color of light, to send information thru the same media using different colors. For the speed of communication, it is important to investigate if these gain membranes delayed the response from the pump. In these experiments the II-VI heterostructure layers were transferred to the sapphire window of a GaN LED. Almost no difference was observed between the frequency response of the LED and the hybrid structure (See figure #7.10), concluding that no delay in frequency response was induced by the application of the II-VI membranes, and these II-VI color conversion membranes are suitable for optical communications.

For more information on the demonstration of the removal of our SDL structures from their grown substrate to other substrates and our SDL structure investigations see Refs. [83 and 153, respectively].

7.5 Conclusions

Two Zn\textsubscript{x}Cd\textsubscript{y}Mg\textsubscript{1-x-y}Se-based MQW structures designed for optically-pumped vertical emission were grown by MBE. Their structural properties were characterized using HR-XRD and SEM. Sharp and well resolved XRD peaks with multiple satellite peaks for the multilayers confirmed their good quality, with small variations between the desired and measured values of layer thicknesses. Their optical spectroscopic properties were studied using steady-state PL,
intensity-dependent PL, and TRPL measurements. Reasonable agreement in the composition of the alloys with the design value was obtained, demonstrated by steady state PL. When the intensity of the pump was varied we saw a sub-linear increase for the PL maximum at 547 nm for sample A and at 539 nm for sample B, for pumping power below 8 mW and 3 mW, respectively. Above those powers the maximum of the PL shifted to 568 nm for sample A and 548 nm for sample B and exhibited a much higher rate of increase in intensity with pump power. Time-resolved studies indicated that the PL at low pump power is mainly due to spontaneous emission and that at high pump power the red-shifted PL maximum is likely due to ASE or to stimulated emission. The sample with the DBR layers (Sample B) showed higher surface PL than the one without the DBR layers (Sample A). A 20-period DBR structure was also grown and its reflectance properties investigated. We observed ~84% reflectivity from this structure, and we estimate that approximately 40 periods will be needed to achieve the desired 99.9% reflectance suitable for a standard SDL structure. These results illustrate the potential of the ZnCdMgSe-based materials for fabricating optically-pumped green light emitting SDLs. Finally, a procedure to remove the layers from their grown substrate, and bonding to alternative substrates was demonstrated. The use of these II-VI layer membranes as color converters was explored.
Chapter 8

Summary and proposed future work

8.1 Summary of this dissertation

In this dissertation we have shown that, using the MBE growth technique, we can achieve ZnCdMgSe-based materials with new and enhanced properties, as well as novel photonic devices with performance that that cannot be achieved by other materials. We discussed the entire process, from the material optimization, to deposition of novel “strain engineered” materials, to the realization of several useful advanced devices with new and improved properties. Here I give a summary of the key findings presented in each chapter.

In chapter 3 we reported on the characterization by CER of a three coupled quantum well structure such as the one employed in the QC lasers grown in our lab, and compared the results with the electroluminescence of a full QC laser device. PL and simulations of the structure were used to identify all of the transitions found by CER. Excellent agreement was obtained when we compared the transitions measured in CER of the test structure with the transitions measured in FTIR absorption from the full QC laser structure. This gave us confidence that 1) we could fully characterize the structures using test samples by using the CER technique, 2) that all the electronic levels that were required for an active region were there, and 3) that we have good parameters to model the ZnCdSe/ZnCdMgSe quantum systems.

In chapter 4 we reported on the investigations of improving the interface quality of MBE grown heterostructures of ZnCdSe and ZnCdMgSe. The incorporation of 20 seconds growth interruptions at each layer interface led to the reduction of the PL FWHM in MQW samples, and in a QC laser core. A direct comparison of a QC laser device grown with and without growth
interruptions in its core, demonstrated large improvements in the electroluminescence intensity and width for the one that was grown with interruptions. From these results growth interruptions have been implemented in the growth of all the structures and devices subsequently grown.

In chapter 5 we relied on strain engineering to be able to use CdSe (the lowest bandgap material within the ZnCdMgSe family) in order to increase the CBO and achieve shorter wavelength intersubband transitions, as well as visible QW emitters emitting in the red region on InP substrates. We demonstrated the realization of these novel materials, and confirmed their excellent structural quality. QW PL emission was obtained from 600-700nm, covering from visible orange to red. Intersubband absorption was measured from 3.83 to 2.56 µm, which are difficult-to-reach wavelengths when using the lattice matched ZnCdSe QW layers, and impossible to reach with the commercial InGaAs/InAlAs material system. We also predict, by simulations and experimental verification, that this system can reach wavelengths as short as 2.1 µm when a 3.0eV ZnCdMgSe barrier is used. We expect that the ZnCdMgSe-based system lattice matched to InP substrates could then reach even shorter wavelengths by using higher barrier bandgaps, making it useful for applications from the near to the far infrared.

Chapter 6 discusses the demonstration of a novel detector: a ZnCdSe/ZnCdMgSe photovoltaic quantum cascade detector (QCD). We first demonstrated QCD operation using a structure designed to be a QC laser. This detector operates in two spectral bands around 2.6µm (low intensity) and 3.6 µm (highest intensity), which correspond to the expected transitions in the QC laser active region. Although calibrated blackbody measurements yield a low peak responsivity of 0.1mA/W at 80 K, background radiation limited infrared performance (BLIP) detectivity of 2.5x10¹⁰ Jones was obtained. A non-optimal extractor design was predicted to be
reason of the low responsivity. The high-bandgap of the II-VI materials proved to be a good property for the devices, indicated by the ultra-low Johnson noise in the detectors.

We then focused on obtaining broadband detectors from the II-VI material system. We optimized the design as a QCD, and grew the first generation broadband detector by stacking 3 different cores in one sample. The responsivity of our detectors improved and the response was broader, but most of the activity was in the top detection core (the shortest wavelength). Further improvements were realized by implementing a new design for the active core (interleaved design). From our results we conclude that the interleaved design is an easy arrangement that yield activity from the both cores, and therefore broadband activity.

We conclude chapter 6 with the experimental results of the optimized room temperature, II-VI, ZnCdSe/ZnCdMgSe, broadband QCD. Two interleaved active absorption regions centered at wavelengths 4.8 um and 5.8 um were employed. A broad and smooth photocurrent spectrum between 3.3 µm and 6 µm spanning a width of 1030 cm\(^{-1}\) measured at 10% above baseline was obtained up to 280 K, corresponding to a ΔE/E of 47%. Calibrated blackbody responsivity measurements show a measured peak responsivity of 40mA/W at 80 K, corresponding to a detectivity of 3.1x10\(^{10}\) Jones.

A different photonic device, this time based on interband transitions in the visible range, is presented in Chapter 7, which discusses the structural and optical properties of multiple quantum well (MQW) structures and distributed Bragg reflector (DBR) on InP substrates needed for the realization of optically pumped semiconductor disk lasers (SDLs) operating in the green spectral range. We grew and studied a MQW gain structure without a DBR, one with a partial DBR between the gain region and the substrate, and one of a 20 period DBR structure alone. Under pulsed excitation both MQW samples exhibited features of amplified spontaneous
emission (ASE) or stimulated emission in the green region (540nm). This was accompanied by luminescence lifetime shortening. The sample with the DBR showed higher surface luminescence and the onset of ASE at lower pump power. The 20-period DBR exhibited a reflectivity of 83% at 560 nm. We estimate that a DBR with 40 periods would be needed for optimal performance in a SDL using these materials. Lasing form the edge of cleaved cavities was achieved from both samples, corroborating that the ZnCdMgSe material is suitable for these optical devices and is able to close the visible light gap in the green region.

Our collaborators in the UK, using epitaxial lift-off, were able to remove the absorbing substrate and transfer the structure on to transparent substrates. Edge-emitting photoluminescence measurements demonstrated no observable strain relaxation effects or significant shift in comparison to unprocessed samples. Samples capillary-bonded epitaxial-side to glass exhibited a redshift under optical pumping corresponding to a temperature increase in the pumped region; whereas those bonded to diamond exhibited no shift in QW emission, and thus efficient transfer of the heat is achieved (an important factor for SDL). These steps are needed for the final demonstration of the full SDL which is in progress. These samples were also coupled with gallium-nitride (GaN) light-emitting diodes (LEDs) as wavelength converters for optical communications using visible light. The goal was to extend the wavelength coverage of GaN LEDs without compromising their modulation properties. The ZnCdMgSe-based membrane was liquid-capillary-bonded directly onto the sapphire window of a 450 nm GaN micro-sized LED (micro-LED) for full hybridization. No significant change in the modulation properties of the LED were obtained when the color conversion membrane was used, highlighting the good properties of this hybrid II-VI/III-N device.
8.2 Proposed future work

The results shown in this thesis demonstrate that the ZnCdMgSe-based system can be used successfully to address some of the needs in current technologies. Although there is always room for further material quality improvement, our MBE growth of these materials has been optimized to do many wonderful things. I would say we have only scratched the surface of the ways in which these materials could be utilized. Here, based only on the topics I presented above, I will list some unanswered questions and topics that I find exciting and that could be explored further.

In terms of growth interruptions the investigation of the optimum time of the interruption and its effect on the structure has not been answered. We implemented 20 seconds of growth interruptions in our first implementation, and the growth improved significantly. Do we get the same effect if we only do 10 seconds? Does the interface becomes better is we leave the growth interrupted less or more time?

The strain compensated ZnCdMgSe/ZnSe/CdSe symmetric QW system is ready to be incorporated in QWIP devices. The work presented here could easily yield QWIPs that detect in the hard to reach 2-4 µm range. We can also now design and simulate the coupling of two of the ZnSe/CdSe strain engineered asymmetric quantum wells to be grown and used as QC laser active region.

![Figure 8.1: Configurations to be considered to create a two asymmetric quantum well system to be used as a short wavelength QC laser active region.](image)
regions. The addition of these novel materials leave us now with a designer playground. There are many ways on which these quantum wells can be coupled. Some examples are illustrated in figure 8.1.

Simulations can be made to design active regions for intersubband devices. QC detectors active regions can be made to reach the near IR. We can make our QCDs broader by expanding to the short wavelengths.

For the broadband QC detectors I propose that it should be possible to incorporate more cores with the interleaved design to achieve much broader detection. Of course, we should investigate if there is maximum number of cores that can be interleaved. Also it is of interest to me to investigate whether we can separate the cores (in terms of central wavelength operation) and achieve a smooth response. For example, a 1μm separation worked for us for a smooth response between bands. Does a 1.5μm separation works also? Finally, many techniques can be incorporated to enhance the responsivity, such cavity enhancement, or plasmonic antennas to couple other polarizations. Also designs should be made with higher barriers (keeping the same active wavelength). By burying the transitions deeper in the material we can explore whether $T_{BLIP}$ is enhanced.

For the SDLs (or VECSELs) we need to develop full 99.99% reflectivity DBR with ease to be able to tackle this device and achieve vertical emission. One big problem we face with the growth of SDLs is the variation of temperatures during the growth, which made the growth of these DBRs, which take long periods of time, very challenging. Also throughout the structure a several cell temperature changes were made during growth because these SDL structures are made from 4 different material compositions (three different types of ZnCdMgSe quaternaries, and ZnCdSe for the wells). These changes of temperature may produce problems in the growth,
since the fluxes may not have time to stabilize. A way to tackle this problem is the use of short period superlattices (SPSL) instead of random alloys. These have been investigated by others in our group. I propose that instead of using MgSe, we make the SPSL with the lattice matched ZnCdSe, and the highest ZnCdMgSe composition to be used. In our case, that was the 3.0eV bandgap ZnCdMgSe. By using SPSLs we can make several kinds of pseudo-alloys with only two materials, and avoiding the changes of temperature while growing. Finally, for the substrate removal work, or membrane work, we should investigate the incorporation of “sacrificial layers”. Layers that etch faster, such MgSe can be incorporated between the III-V and II-VI layers for subsequent layer lift-off.

The possibility of developing two color SDLs lasers all lattice matched to InP is also interesting. For this we could combine the green emitting QWS with the strain compensated CdSe/ZnSe QWs emitting in the red. Resonant periodic gain can be kept in the same cavity for green and red QW emitters. Several samples have been grown with both types of QW (see figure #8.2).
In terms of Intersubband devices I believe that we are very close on the realization of a QC laser. Optimized optical waveguide structures could be grown. Heat management of the device should also be improved. It is very possible that the quaternary layers are not such good thermal conductors, and this might be the reason for the additional broad peak around 1000 cm\(^{-1}\) in electroluminescence. Measurements of our device should be made at colder temperatures than 77 K.
Publications and Presentations

PUBLICATIONS

First author publications


Other publications


PRESENTATIONS BASED ON THIS DISSERTATION WORK


Bibliography


of a Zn$_{x}$Cd$_{1-x}$Se/Zn$_{x}$Cd$_{y}$Mg$_{1-x}$Mg$_{1-y}$Se asymmetric coupled quantum well structure”, Journal of Alloys and Compounds 509(9), 3751-3755, 2011.


