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Doping and electron-stimulated desorption of zinc selenide grown by molecular beam epitaxy

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**DOPING AND ELECTRON STIMULATED DESORPTION OF ZINC
SELENIDE GROWN BY MOLECULAR BEAM EPITAXY**

THESIS

Submitted to the Eberly College of Arts and Sciences

at

West Virginia University

In Partial Fulfillment of the Requirements for the Degree of

Masters of Science
in Physics

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2002

Keywords:

ZnSe, Molecular Beam Epitaxy, Doping, Electron Stimulated Desorption

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Electron irradiation during reflection high-energy electron diffraction is shown to affect the growth of ZnSe and ZnMgSe by molecular beam epitaxy. The high-energy electrons produce an electron stimulated desorption effect during growth of ZnSe, which primarily affects adsorbed Se. Se desorption rates under electron irradiation are shown to be significantly larger than thermal desorption rates. Electron irradiation also decreases ZnSe growth rates under Zn-stable conditions. The decrease in growth rate can be suppressed by either growth under Se-stable conditions or by using high index substrate orientations, in this case (211)B. High-energy electron irradiation does not alter composition during the growth of ZnMgSe.

ZnSe and ZnMgSe chlorine-doped epitaxial layers were grown in conjunction with computational modeling to investigate solubility, native defects and chlorine-impurity-related defects. ZnSe was found to incorporate Cl at levels up to $2.5 \times 10^{20} \text{ cm}^{-3}$, but was only electrically active at levels up to $1 \times 10^{19} \text{ cm}^{-3}$ with compensation occurring beyond this point. ZnMgSe alloys have a higher Cl solubility than ZnSe, increasing the rate of incorporation by an order of magnitude for the same ZnCl_2 flux. While reflection high-energy electron diffraction images degraded only at the highest Cl source temperatures, growth rates were seen to decrease for a larger range of chlorine fluxes. Compensation appears directly coupled to the reduced growth rate. The lattice constant increased significantly in ZnSe for chlorine concentrations above $\sim 4 \times 10^{19} \text{ cm}^{-3}$.

ZnSe layers were grown by molecular beam epitaxy to study Cr incorporation with the long-term goal of demonstrating an alternate route for achieving transition metal-doped lasers. Concentrations between 10^{15} and $4 \times 10^{20} \text{ cm}^{-3}$ were achieved. Secondary ion mass spectroscopy concentration profiles strongly suggest that surface segregation and accumulation of Cr occurs during growth. Photoluminescence measurements indicate Cr is incorporated in the optically active Cr^{2+} state up to levels of $\sim 10^{19} \text{ cm}^{-3}$. Electron paramagnetic resonance studies suggest that Cr atoms exhibit collective magnetic behavior even at these levels. X-ray diffraction and reflection high-energy electron diffraction indicate high structural quality is maintained for Cr incorporation at levels up to $\sim 10^{19} \text{ cm}^{-3}$.

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"Research is what I'm doing when I don't know what I'm doing." — *Werner von Braun*.

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CHAPTER I

1. Introduction and Overview

1.1 Introduction

ZnSe is a II-VI compound semiconductor. The wide, direct bandgap of 2.8 eV is ideally located such that the material can be used as a blue light-emitting device. In spite of research on ZnSe and other II-VI semiconductors since the early 1960's, a variety of structural and electronic quality issues prevented their rapid development into laser and light-emitting diodes. In 1991, 3M announced that they had built a blue laser out of ZnSe. However, the device required cryogenic temperatures and succumbed to catastrophic optical damage in a very short time. In January 1997, Sony was able to operate a room temperature ZnSe laser for 101 hours. Shortly thereafter, the benchmark for room temperature operation was set by a gallium nitride diode laser, switching the emphasis for the development of blue emitters from II-VI to III-V compounds.¹

Recent advances in ZnSe-based laser materials have focused on ternary and quaternary compounds. The use of alloys such as ZnMgSSe,² ZnMgCdSe³ and CdZnSSe⁴ allows for better lattice matching with III-V substrates in multiple quantum well laser structures. ZnMgBeSe has been used in blue-violet and UV detectors.⁵ The use of CdZnSSe quantum wells has recently exhibited cw-lasing emission at 560 nm.^{4,6} Use of these quaternary compounds also allows tailoring of the bandgap, for example from 2.1-3.3 eV for ZnMgCdSe,⁷ and therefore tailoring of the emission wavelength.

Additionally, growth of single crystal ZnSe using seeded physical vapor transport in 1991 by Eagle-Picher has made ZnSe substrate material available for growth. The Bridgeman method has also been used to make ZnSe substrate material.⁸ The use of ZnSe substrates eliminates the need to tailor the lattice constant to III-V substrates.

There are a number of other issues affecting production of devices. Doping levels are limited to $2 \times 10^{19} \text{ cm}^{-3}$ for n-type material doped with chlorine and $1 \times 10^{18} \text{ cm}^{-3}$ for p-type material doped with nitrogen.^{9,10} Both types of material are subject to compensation with increasing incorporation of dopants. Material degradation occurs from interface defect propagation.

II-VI materials have been investigated as host materials for incorporation of a number of transition metal ions that allow for laser operation in the 2 to 5 μm spectral range.¹¹ ZnSe has been shown to be one of the most promising hosts for room temperature operation using chromium as a dopant. ZnSe:Cr has been investigated through paramagnetic resonance^{12,13} and photoluminescence¹⁴ since the early 1960's as part of a broad investigation into II-VI crystals. Although most research focused on the use of II-VI materials to produce laser diodes based on a p-n junction, high power, optically pumped transition metal-doped zinc chalcogenide lasers have been demonstrated.¹¹ ZnSe:Cr was chosen based on convenient absorption spectra for optical pumping, emission lifetime and quantum yield which showed the most favorable characteristics for room temperature lasing.

1.2 ZnSe: Basic Properties

ZnSe forms in both wurtzite and zincblende (sphalerite) structures, although the wurtzite is metastable. Material grown on GaAs nucleates in the zincblende structure, which is illustrated in Figure 1-1. Zinc and selenium exist on face-centered cubic (fcc) lattices offset by one-fourth the body diagonal. Each zinc (selenium) atom is surrounded tetrahedrally by four selenium (zinc) neighbors, so the structure has four-fold coordination. The bonding in ZnSe is partly ionic as each Zn (Se) contributes two (six) electrons. The energy band structure for ZnSe is shown in Figure 1-2 (without spin-orbit interaction). The direct bandgap is 2.70 eV at room temperature and 2.82 eV at 4.2K between Γ_1 and Γ_{15} . A summary of the general properties of ZnSe is given in Table 1-1.

1.3 Summary of Prior Electron Stimulated Desorption Results

Farrell *et al.*¹⁵ have found that Se atoms are desorbed from ZnSe via a thermally activated electron stimulated desorption (ESD) process. They were able to determine a thermal activation energy of ~ 0.6 eV for the ESD process from 10 keV electrons in ZnSe by timing the disappearance of the twofold reconstruction along the [010] direction for multiple substrate temperatures. The Se-stabilized [010] ZnSe surface exhibits either a (2 $\times$ 1) or a (1 $\times$ 1) reconstruction with an additional two-fold reconstruction along the [011] direction. The Zn-stabilized surface always exhibits a c(2 $\times$ 2) reconstruction.¹⁶ A reconstruction is a consequence of the surface attempting to lower its energy by

Figure 1-1 Lattice structure of zincblende ZnSe.

Figure 1-2 Energy band structure of ZnSe.¹⁷

Property	Value
Lattice parameter	(zincblende) 5.668 Å (wurtzite) a=4.01 Å, c= 6.54Å
Bandgap	2.70 eV (300K) 2.8218 eV (4.2K)
dE_f/dT	$-5 \times 10^{-4} \text{ eV K}^{-1}$
dE_g/dP	$7 \times 10^{-7} \text{ eV cm}^2 \text{ kg}^{-1}$
electron effective mass	0.13
heavy hole effective mass	0.78-1.09
light hole effective mass	0.145
Electron mobility	$200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Hole mobility	$20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$
Dielectric constant	$\epsilon_r = 7.1$ $\epsilon_\infty = 5.4$
Thermal conductivity	$0.19 \text{ W cm}^{-1} \text{ K}^{-1}$
Thermal expansion coefficient	$7.0 \times 10^{-6} \text{ K}^{-1}$
Molecular Weight	144.34 amu
Density	5.42 g cm^{-3}
Melting Point	1520 °C
index of refraction @ 0.680µm	2.565
LO phonon	32 meV
Ionic Radii	$\text{Zn}^{2+} 0.88 \text{ Å}$ $\text{Se}^{2-} 1.98 \text{ Å}$

Table 1-1 Summary of general properties of ZnSe (at 300K unless otherwise noted.)¹⁸

eliminating dangling bonds. Reconstructions come from a surface structure with a larger periodicity than that of the bulk material, which yields a diffraction pattern with narrower spacing than the fundamental diffraction pattern. Observation of the surface reconstruction gives a better grasp of surface stability during growth. Electron irradiation was shown to increase Se-desorption from ZnSe on a scale that can significantly contribute to the growth rate at higher temperatures or slower growth rates. Farrell *et al.* attributes the ESD process to the generation of holes in ZnSe. According to Marfaing¹⁹ the generation of holes will affect the more electronegative surface specie, in this case Se.

Simpson *et al.*²⁰ argues that this same process is the underlying origin of photon stimulated effects observed for above bandgap light illumination during growth. They observed bright cathodoluminescence from a RHEED beam while growing iodine-doped ZnSe. The inelastic scattering of high-energy electrons in the sample results in the generation of an electron-hole population, followed by pair recombination. It is reasonable that both light stimulated desorption (LSD) and ESD are due to the same mechanism because carriers are responsible for desorption in both processes and both are thermally activated.

As the same process occurs for ESD and LSD it is important to consider LSD effects when exploring possible effects of ESD. For the case of above bandgap irradiation, the influence of light on crystal growth includes diffusion related photo-enhanced processes, nucleation and desorption of surface atoms. For MBE grown ZnSe²¹ the growth rate tends to decrease under above bandgap light illumination during growth, unlike MOVPE grown material.^{22,23,24} The growth rate further decreases with increasing temperature indicating that the process is also thermally dependent. In addition, Matsumura *et al.*²¹ investigated desorption of Zn and Se from the physisorbed state and deduced that the desorption constant is higher for Se than Zn, and both increase under photo-illumination. Thus, photo-enhanced desorption has a greater probability for Se than Zn metal. The primary effect of irradiation is reduction of Se coverage via re-evaporation thereby reducing Se in the physisorbed state. Simpson *et al.*²⁰ showed this occurs through the difference between the irradiated growth rate and a low post-growth photo-etch rate. This significant difference will only occur when one of the species is primarily responsible for desorption effects. Most analysis in the literature reviewed by

Marfaing¹⁹ involves direct interaction of photons with the electronic or vibrational states of the adatoms. This applies to molecules physisorbed on metals. However, he also says that the transfer of photo-generated carriers to adatoms would appear to play a prominent role for chemisorbed species. Under light excitation, photo-generated carriers move towards the surface by diffusion and drift across the surface potential barrier. For n-type ZnSe the surface field accelerates the holes to the surface. Desorption of physisorbed adatoms occurs above a certain excitation level. The generation of holes will affect the more electronegative Se.

The metal-stable surface results in greater surface mobility leading to improved crystal structure and enhanced free-exciton emission. Illumination also allows for growth at reduced temperatures, at 150 °C under 300 mW cm⁻² bandgap illumination versus 340 °C under optimal growth conditions.²⁵

For unintentionally doped MOVPE grown ZnSe, the material was found to be more conductive when grown under light excitation suggesting photo-enhanced solubility of residual donors.²⁶ This study also reported increased doping efficiency of I donors and N acceptors. A more in-depth study of CdTe doped with In²⁷ shows that carrier concentration increases with illumination power density for both doped and undoped material. Temperature-dependent photoluminescence leads to the conclusion that light irradiation reduces the compensation of the dopant impurities. Marfaing¹⁹ concludes that the concentration of metal vacancies decreases with increasing light intensity, because of the increase of surface mobility, thereby reducing compensation.

1.4 Summary of ZnSe:Cl

ZnSe and Zn_{1-x}Mg_xSe continue to be of interest because of potential optoelectronic applications. There has been a great deal of work focused on the role of defects and defect complexes in ZnSe with n-type and p-type doping.^{28,29,30,31} Many of these defects can act as compensating centers, reducing the maximum achievable carrier concentration to 2x10¹⁹ cm⁻³, with one apparently unreproducible report of 3x10²⁰ cm⁻³.³² Theoretical results have shown that the substitutional-chlorine-zinc-vacancy complex is the most probable candidate for the compensating center in the case of chlorine doping in ZnSe.³³ Saarinen *et al.*³⁴ recently identified zinc vacancies in n-type ZnSe:Cl using

positron annihilation experiments. The defect complex $\text{Cl}_{\text{Se}}\text{-V}_{\text{Zn}}$ is believed to be formed in heavily Cl-doped ZnSe,^{35,36} and it has even been suggested that the concentration of the zinc-vacancy is of the same order of magnitude as that of four-fold coordinated Cl which is incorporated into the Se lattice site.

The addition of magnesium to form $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ increases the bandgap, lowers the index of refraction,³⁷ and allows tailoring of the lattice constant. These properties make $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ attractive for heterostructure devices where optical or electrical confinement is desired. Calculations by H. Okuyama *et al.*³⁸ show an increase of band gap in $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ from 2.6eV for ZnSe to 3.7eV for MgSe (for the zincblende structure) in close agreement with their quoted experimental values of 2.7eV and 3.6eV, respectively.

Chlorine, as the most successful n-type dopant in ZnSe, is also the best candidate for n-type doping in ZnMgSe. However, experimental results have been disappointing. The data by Ferreira *et al.*³⁹ indicate that the highest electron concentration decreases with increased Mg content in ZnMgSe. In particular, they suggest that the solubility of chlorine decreases with the addition of Mg. Therefore, to gain an understanding of the issues involved, our collaborators used the *ab-initio* full potential linear muffin-tin-orbital method to model native defects and chlorine-related defects in ZnSe and $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$. They focused on the changes in electronic properties with increasing Mg content. These results will be summarized in Chapter 4.

1.5 Summary of ZnSe:Cr

The incorporation of transition metal ions into a semiconductor host is an effective technique for producing material useful for fabricating lasers. In particular, the small crystal field splitting found for transition metal ions in II-VI materials allows for laser operation in the spectral range of 2 to 5 μm .¹¹ Lasers based on these materials are of interest for commercial and military applications for optical identification of chemicals. Many molecules have strong and unique absorption spectra in the infrared. As examples, H_2O , CO_2 , CO , N_2O and HCN can be accurately detected with lasers operating in the mid-infrared.^{40,41} The incorporation of chromium into ZnSe produces an infrared laser material that operates at room temperature and is tunable from about 2 to 3 μm .⁴² Of technological interest, the absorption band which produces the laser emission occurs at

about 1.8 μm . This wavelength is currently accessible using commercial strained layer InGaAsP diode lasers. The Stokes shift between absorption and emission bands is over 1000 cm^{-1} and thus provides a wide emission window from 2.2 to 3.0 μm , where a small degree of self absorption exists.⁴³ In principle, a compact and efficient laser diode-pumped tunable solid state laser can be built. Cr substituting on the Zn site of the tetrahedrally-coordinated II-VI lattice results in a $3d^4$ electronic configuration, often referred to as Cr^{2+} by the community,¹² and is the desired electronic configuration to allow laser fabrication.

1.6 Research Objectives

The development of ZnSe based opto-electronic devices has been limited by compensation and crystal structure degradation at high doping levels. To overcome these obstacles it is necessary to investigate any parameter that may have beneficial effects during growth. Photo-assisted MBE has been used for improving structural and electrical quality in II-IV semiconductors. As high-energy electrons were found to exhibit similar effects as photons during film growth, it seems that they may induce similar improvements in films grown under electron irradiation.

What are the effects of electron stimulated desorption on static and growing ZnSe films? What effects are seen during growth of ZnMgSe films? Does electron stimulated desorption affect point defect formation during growth of ZnSe and ZnMgSe?

Data obtained from ZnSe:Cl and ZnMgSe:Cl has generally been correlated to ZnCl_2 source temperature in the literature. This makes comparison of results from different groups difficult. By making comparisons of SIMS results and data collected in this study it should be possible to “normalize” results to make valid comparisons. This will give better insight into the problems being addressed.

What are the electrical and optical effects of point defects that arise with Cl doping in ZnSe and ZnMgSe? Do experimental results correlate to modeling predictions for Cl solubility and lattice spacing changes? What are the effects of the Zn/Se flux ratio and electron irradiation on defect formation? Is the drop in growth rate seen with heavy Cl-doping directly related to the incorporation of compensating defects? Does substrate

orientation, (100) or (211)B GaAs, affect Cl defect formation as seen by a drop in growth rate?

ZnSe:Cr lasers have been demonstrated using Cr-implanted bulk ZnSe. Epitaxial growth of ZnSe:Cr on GaAs should allow for production of integrated structures.

The first step is to determine whether it is feasible to grow ZnSe:Cr layers by molecular beam epitaxy. Does Cr incorporate in the desired charge state? This can be investigated through photoluminescence and electron paramagnetic resonance measurements. Eventual final goals are covered in the future work discussion in Chapter 5.

CHAPTER II

2. Experimental Equipment

With the development of high performance opto-electronic, electronic, and photonic devices from compound semiconductors and the advancement of ultra-high vacuum (UHV) environments in the 1960's, molecular beam epitaxy (MBE) was developed in the 1970's as a sophisticated deposition technique. It distinguishes itself through precise control of beam fluxes and deposition conditions. This epitaxial growth process involves the reaction of multiple thermal beams of atoms or molecules with a crystalline surface under UHV conditions. The UHV environment allows collimated beams of highly purified source material to arrive at the substrate without colliding with other atoms or molecules, minimizing contamination. The heated substrate surface allows the arriving atoms to distribute themselves evenly across the surface, minimizing imperfections in the crystal structure. These conditions generally give better control of the growth through kinetics of surface processes between the impinging beams and the substrate than other growth methods (e.g. MOCVD and VPE.) Almost any material composition and doping level can be achieved through the use of shutters and precise control of effusion cell temperatures. Accurate control of incident fluxes permits modulation of composition down to atomic layers. This tight control of dopant profiles, layer thickness and minimization of contaminants contribute to exceptional optical and electrical properties.^{44,45}

2.1 MBE System

The MBE system used in these studies was designed and built in the Physics Department at West Virginia University for the growth of II-VI and III-V semiconductors. The system consists of a load lock for sample introduction and a main chamber for sample growth. The chambers are constructed from stainless steel and isolated by gate valves.

When the main chamber has been vented using ultra high purity (UHP) nitrogen, it is first pumped down to 10^{-6} Torr using the turbo-molecular pump (Varian Turbo-V250 pump)(TMP) through the load lock chamber. Then the gate valve between the load lock and main chamber is closed and the main chamber pumping is taken over by a CTI-

Cryogenics CT-8 cryopump. A vacuum of $\sim 10^{-8}$ Torr is obtained. A bakeout of the main chamber at elevated temperatures of 100-120°C is necessary to desorb atmospheric gases from the chamber walls. After bakeout, a typical vacuum in the main chamber is about 10^{-9} Torr, which decreases to the low 10^{-10} Torr range upon introducing liquid nitrogen into the cryoshroud. During growth, typical background pressure is 10^{-8} to 10^{-9} Torr depending on growth conditions.

The sample block is introduced into the main chamber via the load lock. First, the sample block must be placed into the load lock. The load lock is isolated from the main chamber and the TMP using gate valves, then vented with dry, UHP nitrogen gas. The sample block is then inserted, and the load lock can be pumped down to 10^{-6} Torr in about 30 minutes. The gate valve between the load lock and growth chamber is then opened, and the sample block is transported between the two chambers using a transfer arm. Once inside the growth chamber the sample block is then transferred to the substrate manipulator, the transfer arm is withdrawn and the gate valve is closed.

2.1.1 Chamber and Source Flange

The main chamber consists of a 14" diameter cylinder with a hemispherical top that contains the substrate manipulator. The chamber sits on the supporting frame inclined 30° downward with respect to the horizontal. This permits the use of liquid source material, which would be precluded in the upper source ports if the chamber were not inclined. Ports that should be noted are those used for the reflection high-energy electron diffraction (RHEED) setup and the windows used for reflectance interferometry. The ports for the RHEED setup are lined up on opposite sides of the chamber diameter. A 4.5" flange port holds the RHEED electron gun. The opposite 8" flange port contains the fluorescent screen for the RHEED diffraction pattern display. Two 4.5" flange ports on opposite sides of the chamber, 35° off the chamber wall, aimed at the sample center, are used for laser reflectance interferometry. A third 4.5" flange port houses the hydrogen source used for *in-situ* cleaning of the substrate prior to growth. The chamber contains additional ports of various sizes to allow for expansion of growth and characterization capabilities. The chamber is equipped with an ion gauge for measuring system pressure and a beam flux monitor (BFM) which can be placed in the beam path to

measure source flux in front of the substrate. The substrate manipulator also contains the substrate heater assembly. The manipulator can be adjusted in all three dimensions, as well as allowing for rotation in the plane of the substrate.

A liquid nitrogen cooling shroud, which is designed to surround the substrate block to take the heat load released by the substrate heater, is shown in Figure 2-1. The shroud has a 4-liter liquid nitrogen capacity and fills with liquid N₂ through an inlet connected to a 20-liter liquid nitrogen tank that is located next to the main chamber. The temperature at the Molybdenum plate is monitored by a thermocouple welded to the front surface of the plate. This controls a solid state relay, which activates a solenoid valve to vent nitrogen gas and let liquid in when the temperature is above the set point. The temperature at the Molybdenum plate is normally held at -100 °C when the shroud contains liquid nitrogen. Similar to a cryotrap, the substrate shroud also serves as an additional pump to the vacuum system, especially for water and carbon dioxide.

The source flange houses the source ovens and individual shutters for each oven. Figure 2-2(a) shows an air-side view of the source flange. Figure 2-2(b) shows the current configuration of the source ovens.

A two-part cooling shroud is used for cooling the ovens. The ovens are isolated from each other in the lower shroud by stainless steel walls. The inner cavity is cooled by circulated water held at 9 °C using a NESLAB HX-200 cooling system. The top shroud is a stainless steel double wall container with an opening on its top connected to the lower shroud to further disperse heat from ovens. There is a narrow gap between the upper and lower cooling shrouds. Oven shutters are set in front of each oven just above the opening on the lower shroud. Shutters operate independently of each other with the shutter feedthroughs located near each oven, except for the Cr oven. For the Cr source, the shutter feedthrough passes through the oven's flange. An overall source shutter is set in front of the top shroud opening. The distance between the front of the sources and the substrate surface is about 30 cm.

After loading new source material into the system, the chamber needs to undergo a bakeout, and the ovens are outgassed at elevated temperatures. Prior to the first growth using newly loaded source material, the source is run with a flux higher than the normal

Figure 2-1 Schematic diagram of the substrate cooling shroud.

Figure 2-2 (a) An air-side view of the source flange illustrating where a maximum of seven ovens can be installed. (b) Current configuration of ovens.

growth flux for about two hours to minimize subsequent contaminant incorporation into layers.

2.1.2 Sources

Molecular beams are typically generated using standard MBE-compatible Knudsen cells consisting of a resistive heater assembly surrounding a pyrolytic boron nitride crucible containing the source material with a thermocouple to monitor the source temperature. Temperature stability to about 1 °C is achieved with a feedback loop and a Eurotherm 818 temperature controller (Leesburg, VA USA). The temperature of the source and the vapor pressure of the material are the main factors that determine the flux of material that reaches the substrate. High purity elemental Zn and Se are used as source material (99.99999% and 99.9999%, DOWA International Co. LTD, Japan.) Alloying was achieved using high-purity magnesium (99.9999%, ESPI Ashland, OR USA.) The vapor pressure curves for Zn, Se, Mg, ZnCl₂ and Te are shown Figure 2-3(a). For Zn, Te, Mg, ZnCl₂ and Se, low temperature cells are used because of their high vapor pressure at low temperatures. For Cr, which has a low comparable vapor pressure shown in Figure 2-3(b), a high temperature cell (EPI-6-HT-SP, Applied-EPI, St. Paul, MN) is needed for use at temperatures up to 1300 °C. It consists of a 6 cm³ tungsten crucible held by an alumina liner to minimize potential crucible breakage. The Cr furnace is equipped with a type-C thermocouple, while the others are equipped with type-K thermocouples.

The hydrogen source (EPI-AHS, Applied-EPI, St. Paul, MN) operates by the dissociation of molecular hydrogen into hydrogen atoms. UHP hydrogen (99.9999%) flows into the source (shown schematically in Figure 2-4) through a UHV leak valve and across a tungsten filament that is heated using a DC current to a temperature greater than 1600 °C. Some fraction of the molecular hydrogen is dissociated by a catalytic reaction on the hot tungsten surface resulting in a mixture of atomic and molecular hydrogen being produced by this source.

Figure 2-3 Vapor pressure curves for (a) high vapor pressure elements and (b) chromium.

Figure 2-4 Schematic drawing of the atomic hydrogen source from Applied EPI, Inc.
Saint Paul, MN.

2.2 Characterization

2.2.1 In-situ Techniques

2.2.1.1 Reflection High-Energy Electron Diffraction

RHEED is a very simple, yet powerful and relatively non-intrusive tool used for quantitative and qualitative measurements during growth (some limitations during the growth of II-VI materials are discussed in Chapter III). A standard RHEED set-up is shown schematically in Figure 2-5. A VE-026 electron gun (Vieetech Japan Co., Ltd.) produces a beam of energetic electrons (in this study, 25 μ A at 13 keV unless otherwise noted) that strike the sample surface at a grazing incidence ($1-2^\circ$). The electrons produce a diffraction pattern on a phosphor screen on the opposite side of the growth chamber. A charge-coupled device (CCD) camera captures the screen image for storage and later analysis. Because the RHEED beam is aligned nearly in the same plane as the substrate, the electron gun and camera do not interfere with the valuable area used by sources and detectors that need to be closer to the substrate normal.

The spacing of the lines in the RHEED diffraction pattern can easily be used for determination of interplanar spacing for different crystallographic orientations. RHEED intensity oscillations can be monitored to determine layer thicknesses or beam fluxes.⁴⁶

Due to the grazing incidence of the beam, the electron momentum normal to the surface is kept small, making RHEED a very surface-sensitive technique that only samples the top few monolayers of the film. A variety of diffraction patterns can be seen using RHEED. These depend on, among other things, the crystal symmetry, the surface morphology, and any surface reconstruction that may be present. For example, if the diffraction pattern is made up of long, uniform streaks, the surface is growing smoothly, in a two-dimensional fashion as the electrons are exhibiting true reflection diffraction.⁴⁵ If the diffraction appears in the form of spots, the surface is more three-dimensional and rough, exhibiting transmission-reflection diffraction. The appearance of a ring-like pattern is usually an indication that a sample is polycrystalline.

Figure 2-5 Schematic drawing of the RHEED set-up. Shown are the electron gun, the sample, the phosphor screen and the CCD camera.

Surface reconstructions generally show dependence on incident fluxes and substrate temperatures. Reconstructions can give indications as to which species of adatom is stabilized on the growth surface and the configuration of the stabilized surface, which can affect dopant solubility and placement.

2.2.1.2 Laser Reflectance Interferometry

It is useful to be able to determine the growth rate of the sample as it grows. This allows the effect of a single parameter on the growth rate to be determined while keeping all other parameters identical without having to grow multiple samples. For example, either the effects of changing the Zn/Se flux ratio or the effect of varying substrate temperature on the growth rate could be determined for many conditions in one growth, as will be discussed in the next chapter. *In-situ* determination of growth rate is also necessary to correctly determine the timing of such events as the opening or closing of a dopant shutter. The growth rate measurement involves a pair of viewports, each facing the substrate at a 35° angle from the sample normal. An S1031 5 mW red diode laser (Thorlabs, Inc., Newton, NJ) with a wavelength of 680 nm is directed toward the sample through one viewport and the specular reflection is collected at the opposing viewport with a photodiode. The laser is electrically modulated by use of a square-wave function generator allowing the use of lock-in techniques to eliminate noise from the surrounding environment. An SR850 DSP Lock-In Amplifier (Stanford Research Systems, Sunnyvale, CA) is used to collect interference spectra. A sample spectrum is shown in Figure 2-6. As the thickness of the film changes (i.e. as the film grows), the thin film interference condition for the monochromatic red light sweeps through maxima and minima. Reference samples are grown with a known number of interference fringes, and the thicknesses of these samples are measured *ex-situ* using a standard optical transmittance measurement on a Cary 14 spectrophotometer. Given the thickness and the number of fringes for each of these reference samples, a “growth rate constant” can be found. This constant can also be found using system geometry, optical constants and interference theory. In the current system, one fringe represents approximately 0.136 μm of ZnSe growth. This constant is then used to determine a sample’s growth rate *in-situ* by measuring the period of interference fringes.

Figure 2-6 Laser interferometry growth rate measurement of ZnSe. The time of 10276 seconds over 7 fringes gives a growth rate of $\sim 0.33 \mu\text{m/hr}$.

2.2.2 Ex-situ Techniques

2.2.2.1 Photoluminescence

Exciting a semiconductor with above band gap light produces excess electrons and holes. These excess carriers will find any number of pathways to reach their initial, unexcited state. Many of these recombination pathways will be radiative in nature, meaning that they will emit light with an energy specific to that transition. Photoluminescence (PL) is a powerful technique which can acquire useful information about defects and impurities in the crystal that have formed energy levels in the band gap by analyzing the spectral nature of the emitted light, or luminescence. It can be used for mapping energy levels in the bandgap and determining binding energies of dopants. A phonon replica is the signature of an electron-lattice interaction during the recombination process. It appears as one or more replicas of the main recombination peak displaced by multiples of the energy of the relevant phonon. In compound semiconductors the electron-phonon interaction typically occurs for the longitudinal optical mode phonon, which for ZnSe is about 32 meV.⁴⁷

Photoluminescence measurements were performed in Professor Nancy Giles' laboratory by Lijun Wang, Lihua Bai and Ke Feng at West Virginia University's Department of Physics as part of the collaborative efforts on compound semiconductors. PL spectra were obtained using one of two techniques. Near-bandedge PL was measured using above-bandgap excitation (325 nm at 0.6 W cm^{-2}) from a helium-cadmium laser. A Janis SuperVaritemp Dewar was used to obtain PL data at 5 K. The laser beam was focused on the sample surface and the emitted light was collected in a near-backscattering geometry using a 0.64-m monochromator (model HR 640, Instruments SA) with a 1200 g/mm grating and a GaAs photomultiplier. For measurement of infrared PL, below-bandgap excitation of 514.5 nm at 14 W cm^{-2} from an argon ion laser or 442 nm at 0.35 W cm^{-2} from a helium cadmium laser was used. Note that the bandgap of ZnSe at 5K is $\sim 440 \text{ nm}$. The samples were placed on the cold finger of an Oxford Instruments continuous flow cryostat at 10K. A ThermoNicolet model Nexus 870 Fourier-transform infrared (FTIR) spectrometer was used to collect PL spectra at 10K. A

HgCdTe detector was used to detect the emission from 0.9 μm to 4 μm . Collected spectra were corrected for the response of the detection system.

2.2.2.2 X-Ray Diffraction

X-ray diffraction (XRD) measurements were performed using copper $K\alpha_1$ radiation from an 18 kW rotating copper anode x-ray generator with a four-circle diffractometer. High-precision measurements used a Si single crystal monochromator. Measurements on $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ were done using a focused graphite single crystal monochromator. Lattice constants were determined using the Bond method.⁴⁸

2.2.2.3 Hall Effect

The Hall effect is an efficient and inexpensive measurement of the electrical properties of semiconductors. The sign and density of the majority carriers can be easily determined, as well as their mobility. In addition, temperature-dependent measurements can extract information about impurity energy levels within the band gap and the concentrations of those impurities. This information is essential for the development of semiconductor devices, and is a very useful research diagnostic.

A temperature-dependent Hall effect apparatus is used to perform the electrical characterization of samples grown within this laboratory. Samples are mounted on a custom designed sample holder, and fine wires are soldered to the sample with In or Hg-In using the standard Van der Pauw four-point geometry to provide electrical contact.⁴⁹ Hg-In contacts are annealed at 320 $^{\circ}\text{C}$ for 30 seconds under N_2 to increase Hg diffusion into the sample. This improves the ohmic properties of the contacts. The sample holder is then placed in a Cryomech GB15 cryostat where the temperature is controlled and monitored by a TRI Research Model T2000 temperature controller using a resistive heating element and diode sensors. The cryostat is evacuated to a pressure less than 2×10^{-5} Torr using a Balzers TPU330 TMP station before cooling. The cryostat is placed between the poles of a Varian water-cooled electro-magnet driven by a Hewlett Packard Model 6456B power supply, with a typical magnetic field of 6 kgauss for these experiments. Measurements are possible between 10 and 400K, but are often limited to a minimum of $\sim 100\text{K}$ due to the contacts becoming non-ohmic.

Current is supplied during measurements to the sample by a Keithley Model 220 current source and monitored by a Keithley Model 175A multimeter. The various voltages are then monitored using a Keithley Model 197A multimeter. The current supply, voltmeter, and ammeter are connected using a Keithley 7001 switching unit. This switching unit allows the current to be directed between any combination of electrical contacts, a necessity of the four-probe measurement. The switching unit is connected through an IEEE-488 BUS to a 486 computer for systemization of measurements and calculations of resistivity, Hall coefficient, Hall mobility, and carrier concentration. All electrical leads external to the cryostat are Keithley triax cable.

2.2.2.4 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) measurements were carried out on a number of the samples in this study. All SIMS measurements were performed at Evans Analytical Group, Charles Evans and Associates (Sunnyvale, Ca). A high-energy beam of ions, typically oxygen or cesium, is used to sputter a crater into a sample during the SIMS measurement. The ejected material is analyzed by mass spectrometry to determine what chemical species composed the bulk of the material. In this way, a depth profile is obtained. This type of information is extremely useful when attempting to analyze the incorporation and diffusion of both intentional and unintentional impurities in a semiconductor.

SIMS measurements were made to determine the doping concentration profiles of chlorine in ZnSe and $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ samples using Cs^+ ions. Measurements of chlorine in ZnSe and $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ indicated minimum detectable concentrations were $5 \times 10^{15} \text{ cm}^{-3}$ and $1 \times 10^{16} \text{ cm}^{-3}$ respectively. Chromium profiles were obtained using O_2^- ions. The minimum detectable chromium concentration was found to be $5 \times 10^{13} \text{ cm}^{-3}$. Absolute concentrations were determined using both a chlorine and a chromium standard prepared by ion implantation in a thick MBE ZnSe layer.

Magnesium percentages were determined using direct comparison to a ZnMgSe standard supplied, whose Mg concentration was determined using single crystal X-ray diffraction.

2.2.2.5 Optical Microscopy

Nomarski microscopy is a useful optical method for examining topological features and defects larger than ~ 100 nm. In this technique, two microscopic images of a surface are formed so that they are slightly displaced in space and have opposite phases. Interference bands appear where the images overlap. The physical displacement and the interference bands heighten the visibility of small variations in surface levels. If using an ultra violet (UV) light source for illumination, the above bandgap light will excite electrons to the conduction band and other high energy levels in the band gap. The intensity of the resulting luminescence due to recombination of electron-hole pairs directly reflects the surface structure of the illuminated area and results in a fluorescent image.

An Olympus BMP-60 optical microscope was used to perform the Nomarski microscopy examination of samples for surface features. A 100 W Hg lamp was utilized as the UV light source for fluorescent microscopy.

2.2.2.6 Electron Paramagnetic Resonance

Magnetic resonance is used to obtain information through the effects associated with the spin angular momentum of nuclei and electrons. The electronic structure of single defects is revealed by the fine structure of absorption, and internal magnetic fields are sampled by the spin as revealed by the position of the resonance line.⁵⁰

The electron paramagnetic resonance (EPR) data was collected in Professor Larry Halliburton's laboratory by Madalina Chirila at West Virginia University's Department of Physics. Spectra were obtained using a Bruker Instruments EMX spectrometer operating at a microwave frequency of 9.478 GHz, a static modulation of 100 kHz, a modulation amplitude of 5 G, and a microwave power of 6.36 mW. An Oxford Instruments Model ESR-900 helium-gas flow system was used to control the sample temperature from 4.2 to 30K during the EPR experiments.

CHAPTER III

3. Basic Growth

All thin film growth done in this study follows the same general sequence of events. Each substrate is degreased and etched following a standard procedure, loaded into the vacuum chamber, cleaned with atomic hydrogen, nucleated with zinc and then a standard “buffer” layer is grown before experimental work begins. Although these processes have become standardized for these studies, they evolved from a large effort investigating improving sample quality. The process will continue to change as new advances are made and understanding of factors contributing to the quality of growth occurs. The standardized procedures for a typical growth sequence are described below.

3.1 Sample Preparation

ZnSe and ZnMgSe samples for this study were grown on undoped semi-insulating GaAs oriented either (211)B, or (100) cut 2° toward (110). Use of undoped substrates was particularly important for the Cr-doping studies, as Cr is typically used as a dopant to obtain semi-insulating substrates and this could have obscured EPR studies. The substrate pieces were typically 1 to 1.5 cm squares, with the exception of samples grown as 3 mm wide by 1 cm long RHEED bars. The reason for this sample size is explained in section 3.5.2. Substrates are initially put through a degreasing process. This consists of placing the substrate successively into 80 mL of trichloroethylene, acetone and methanol, each at 80 °C for five minutes. As the substrate is removed from the methanol bath it is sprayed with fresh methanol from a squeeze bottle and then blown dry with UHP nitrogen gas. The sample is then rinsed in deionized (DI) ($>18\text{ M}\Omega\text{-cm}$) water for five minutes and again blown dry with UHP nitrogen gas. Next, the substrate is carefully placed into an acid etch such that it enters the acid mixture parallel with the surface of the liquid to ensure an even etch across the surface. The acid consists of a room temperature mixture of 8:1:1 $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$, contained in a teflon beaker. Immediately after the five minute acid etch, the substrate is removed from the acid bath and dipped in a beaker of DI water, then rinsed in flowing DI water for five minutes and blown dry with UHP nitrogen. The substrate is mounted on a molybdenum substrate block with a thin layer of

indium to ensure good thermal contact with the block. The block is then introduced into the MBE growth chamber via the load lock as described in Chapter 2.

The substrates were further cleaned *in-situ* using atomic hydrogen at a substrate temperature of 400 °C. This cleaning process produces an As-stable surface, which is needed for defect reduction.^{51,52,53} The procedure also removes the oxide layers from the surface at a lower temperature than can be used with only thermal cleaning. Before the hydrogen source is turned on the RHEED power supply is slowly turned on to 13 kV with a 25 μ A emission current. The RHEED pattern usually appears as dim spots or streaks before the hydrogen clean. The hydrogen source is warmed up in 2 A increments to 8 A, with a final step to 9.5 A, which corresponds to a filament temperature of $\sim$ 2200 °C. For this operating temperature about 10% of the resulting flux is atomic hydrogen, which corresponds to a cracking efficiency of 5 to 10 %.⁵⁴ Based on the reported cracking efficiency along with a relative ion gauge sensitivity of 0.5,⁵⁵ we can estimate the actual flux of H atoms. A hydrogen pressure of 2×10^{-6} Torr beam equivalent pressure (BEP) is the pressure read directly on the system ion gauge which is located above and behind the sample manipulator. It is calibrated for nitrogen gas. This pressure corresponds to a flux of approximately 1-2 monolayer/s equivalent of atomic hydrogen at the growth surface. This cleaning process lasts for 20 minutes.⁵³ After the hydrogen source is turned off, the substrate temperature is set to 300 °C, the RHEED pattern exhibits a bright and streaky pattern, usually with Kikuchi lines and a Laue ring of spots.

3.2 Typical Growth Sequence

All solid sources are raised to their growth temperature approximately two hours before the start of a growth. The Zn/Se flux ratio is checked before the growth starts using the BFM, which is placed in the flux path in front of the substrate shutter. The surface is hydrogen cleaned and then approximately twenty to thirty minutes pass while the hydrogen source is powered down and the system pressure drops to $\sim 10^{-8}$ Torr. For a uniform growth the Zn/Se flux ratio is typically set somewhere between 0.75 to 0.5 based on (1) kinetics growths discussed below and (2) indications as to where the Zn-stable to Se-stable transition is, based on reconstructions from the previous growth. This need underscores the observation that BEP ratios for ZnSe growth are at best relative

indicators of growth conditions. To initiate the growth, the substrate shutter is opened and the sample is exposed to Zn for one minute. This process helps to ensure a Zn-stable interface, which along with beginning with an As-stable surface, helps to eliminate nucleation of stacking faults in the material.^{56,57,58} The Se is then opened to the substrate for 30 seconds during which approximately five monolayers of material are deposited on the surface. The RHEED pattern usually turns spotty quite rapidly indicating a roughening of the surface. The Se shutter is closed and the sample is exposed only to Zn for 60 seconds. This procedure, called migration-enhanced epitaxy (MEE), allows adatoms to move around to form a more stable surface. This 90 second process is then repeated. During the last 60 seconds of this process a streaky, Zn-stable reconstruction is usually obtained. Finally, the Se shutter is opened a third time initiating continuous growth. The RHEED pattern usually recovers its streakiness within the first five minutes of growth. If the RHEED pattern hasn't recovered a streaky pattern by this time and cannot be recovered with adjustment of the Zn/Se BEP ratio, the growth is terminated. Once recovered the RHEED beam is moved off of the sample to prevent Se-desorption effects as discussed later in this chapter. The RHEED is returned to the sample periodically to check on surface reconstructions, growth mode and crystallinity of the film.

Closing of the substrate shutter terminates the growth. Substrate temperature is turned down to room temperature and the ovens are set to their idle temperatures.

3.3 Growth Kinetics

Each time source material is added to the system, a “kinetics” sample is grown to calibrate the oven pressures. The Se pressure is held constant at a level that gives the desired growth rate. The Zn pressure is varied and measured along with the growth rate. For Zn-limited (Se-stable) growth conditions, the growth rate increases with increasing Zn pressure. For a Se-limited (Zn-stable) growth, the growth rate remains constant as the Zn pressure increases. These two conditions define the two behaviors of the graph seen in Figure 3-1(a) and (b). To grow under Se-stable conditions the Zn oven temperature is typically reduced by about 5 degrees from that producing the knee in the calibration graph; this generally reduces the Zn/Se flux ratio ~10-20%. The shift from

Figure 3-1 (a) Kinetics growth for BEP calibration versus actual growth rate. (b) BEP calibration normalized to maximum growth rate.

stoichiometric conditions to Se-stable growth is accompanied by the loss of the Zn-stable reconstruction.

Substrate temperature is based on the growth of a kinetics sample, where the growth rate is found relative to the substrate temperature. If the substrate temperature is too high, source material is re-evaporated from the surface. If the substrate temperature is too low, the impinging material does not diffuse on the surface, resulting in a rough surface. The optimum growth conditions consist of the point where substrate temperature effects are balanced with kinetics factors, including the temperature dependence of Se desorption, to maximize the growth rate without losing quality of the RHEED pattern.

DePuydt *et al.*¹⁶ systematically studied the effects of growth temperature (T_G) and Zn/Se beam-equivalent pressure ratio (BPR) on the growth of undoped ZnSe on (100) GaAs substrates using RHEED to monitor the surface reconstruction during growth. They generated a growth matrix as shown in Figure 3-2, in which the Se-stabilized condition and the Zn-stabilized condition were determined by the combination of the growth temperature and BPR. The Zn-stable [Se-stable] condition corresponds to a $c(2 \times 2)$ [(2×1)] surface reconstruction in RHEED. The transition between the two stabilized surface regimes is indicated in Figure 3-2. Meanwhile, another line was defined as the transition from a spotty to a streaky RHEED pattern. It is generally believed that the spotty pattern indicates a three-dimensional growth regime while the streaky pattern indicates two-dimensional growth. The conditions labeled as the optimum line were suggested because the best quality undoped ZnSe samples were grown using the conditions indicated by this line, which correspond to a Zn-stabilized condition with the growth temperature and BPR configuration parallel to the Se-to-Zn transition line. Although the best electrical quality undoped ZnSe occurs for Zn-stable conditions, it has been shown for nitrogen doping,¹⁸ and suggested for chlorine doping,^{39,59} that Se-stable conditions may provide for better doping results.

3.4 Growth of $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ Alloys

ZnMgSe and ZnMgSSe alloys are used as lattice matched cladding layers in the growth of heterostructures such as laser diodes.² A ZnSe based laser was first demonstrated in 1991.⁶⁰ The material was plagued with limited capabilities; one of the limiting factors was the constraint of the lattice parameters of the materials. The lattice

Figure 3-2 Growth matrix of growth temperature and BPR of Zn to Se, which provides growth reference for Zn-stable or Se-stable growth, and spotty or streaky pattern from the growth surface. (Taken from DePuydt *et al.*⁸)

matching capabilities of these alloys, first developed by Okuyama *et al.*,³⁸ introduced viable cladding materials which increased flexibility of II-VI laser diode design and growth. Since the introduction of these materials into optical structures they have been used to achieve quantum confinement in quantum wells, lines and dots.⁶¹

MgSe crystallizes in a rock salt formation, resulting in a critical point for limiting the mole fraction of Mg. This point has been pushed as high as 60% of the molar percentage, but is accompanied by degradation of the crystal quality, which is observed by broadening of XRD rocking curve peaks.⁶¹ There are a number of methods to determine the Mg percentage and sample thickness both during and after growth. We focus on laser reflectance interferometry, XRD and PL, as these have been the methods for making these determinations on our samples.

3.4.1 Laser Reflectance Interferometry

In-situ determination of the growth rate of an alloy as measured by laser reflectance interferometry is influenced by at least three factors. First, the growth rate changes with the addition of Mg, including a change of lattice constant as given in section 3.4.3. Second, the index of refraction changes with the Mg molar fraction as given by:

$$n(x) = 2.565 - 0.466 x + 0.110 x^2 \quad (3.1)$$

for a wavelength of 0.680 μm .³⁷ The third factor is that, while the growth is started Se-stable, the addition of Mg can change the II/VI ratio from less than 1 to between 1 and 2. This is evident from the appearance of the group II-stable surface reconstruction for low Mg concentrations.

Thus, the limited amount of Se available during the growth introduces site competition between Zn and Mg. While the growth rate increases, fewer Zn atoms are incorporated than for unalloyed material with the same Zn/Se flux. The trend in increasing x-value versus growth rate follows a roughly linear increase up to a Mg concentration of about 25% under standard starting conditions. Above this point the growths are severely Se-limited and only a small increase in growth rate is observed for higher Mg molar percentage. This apparent change for severely Se-limited growth is dependent only on the changing index of refraction and the changing lattice constant.

These issues could be alleviated by beginning the growths with a higher Se flux than what is needed for the additional Mg, thereby preserving Se-stable conditions. Without Se-stable conditions, using the change in growth rate to measure composition is unreliable and depends strongly on the (Zn + Mg)/Se flux ratio. In spite of the need for a better calibration curve to locate a BEP ratio, extrapolating growth rate changes based on prior experiments can give a reasonable grasp of the alloy composition during growth. For example, in an alloy-modulated doped structure discussed in Chapter IV, target x-value steps of 0.15, 0.30 and 0.45 were chosen while actual values of 0.16, 0.27 and 0.43 were obtained. Additional effort is needed in this area.

3.4.2 Photoluminescence

PL is typically used to measure the band gap energy and evaluate optical quality. These correlate to the emission peak related to the free exciton transition and the line width of this transition, respectively. The dependence of band gap energy on Mg molar percentage is given at room temperature as:⁶²

$$E_{gap} = (1 - x)E_{gap}^{ZnSe} + xE_{gap}^{MgSe} - 0.1 \cdot (1 - x)x \quad (3.2)$$

where 0.1 is a bowing parameter specific to this alloy, E_{gap}^{ZnSe} is 2.7 eV and E_{gap}^{MgSe} is 3.6eV.

3.4.3 X-Ray Diffraction

X-ray measurements generally determine alloy concentrations with a higher degree of accuracy than PL due to uncertainty in the exciton binding energy and bowing parameter. Lattice constants are measured using XRD from the (400) reflections. Note that for these measurements simultaneous measurement of the GaAs substrate was not performed. Lattice constant dependence on the molar fraction Mg for $Zn_{1-x}Mg_xSe$ is given by the Vegard's law expression:³⁷

$$a(x) = 5.668(1 - x) + 5.89x \quad (3.3)$$

XRD and PL have been used to determine Mg composition for a subset of samples. The comparison is made in Table 3-1.

Sample Number	Mg % (XRD)	Mg% (PL)
01106	0	0
0094	13	10
00107	22	23
00101	26	24
00104	43	45

Table 3-1 Comparison of methods for determining molar fraction of Mg in ZnMgSe.

3.5 Electron Stimulated Desorption

3.5.1 The Effect of Electron Irradiation on Static ZnSe Surfaces

During our studies of the growth of ZnSe, we often observed features on the grown layers that correlated with the location of the electron beam during RHEED measurements. We have sacrificed sample rotation for better knowledge and control of the sample temperature during growth. If RHEED is performed during growth, the samples contain a discoloration in the form of a stripe visible to the eye. Spatial/spectral reflectance imaging was performed at Chemicon Inc. (Pittsburgh, PA.) Such a stripe is readily apparent for the sample shown in Figure 3-3(a), which is a reflectance micrograph taken at a wavelength of 900 nm.

Figure 3-3(b) shows the spectral reflectance taken both inside and outside the RHEED stripe. Analysis of the interference pattern indicates a slight decrease in growth rate with electron irradiation. This leads to a phase difference in the interference of the reflected light in the two regions, and provides the contrast making the stripe apparent.

ESD effects have been previously reported by Farrell *et al.* for ZnSe,¹⁵ and for CdTe by Wu *et al.*⁶³ Electron irradiation was shown to increase Se-desorption from ZnSe and Te-desorption from CdTe static surfaces. In particular, the Se-stabilized (100) ZnSe surface exhibits either a (2×1) or a (1×1) reconstruction with an additional two-fold reconstruction along the [011] direction. The Zn-stabilized surface always exhibits a c(2×2) reconstruction without the additional two-fold reconstruction along the [011] direction.¹⁶ The reconstructions are shown in Figure 3-4. Thus, either the disappearance of the reconstruction along [011] or the emergence of the two-fold reconstruction diffraction along the [010] direction can be used to monitor Se desorption. Without continuous exposure to a Se flux, a Se-stable ZnSe surface under vacuum evolves to a Zn-stable state, indicating this is the more stable reconstruction in vacuum. In order to investigate Se-desorption kinetics we chose to monitor emergence of the [010] reconstruction to indicate the attainment of a Zn-stable surface. After the 0.3 μm ZnSe buffer layer was grown, the growth was interrupted and the static surface exposed to a Se-flux for 5 seconds. The Se shutter was closed and the RHEED pattern was monitored using a CCD camera.

Figure 3-3 (a) Reflectance image of a ZnSe layer at a wavelength of 900 nm. (b) Spectral reflectance from the locations indicated by the rectangles.

Figure 3-4 RHEED reconstructions demonstrating zinc and selenium stable surfaces.

Figure 3-5 indicates the times required after the Se shutter was closed for the emergence of the [010] reconstruction pattern for several substrate temperatures for surfaces under electron irradiation. Each point represents the average of five measurements. The temperature-dependence indicates a thermally activated process, with an activation energy between 0.8 and 1.0 eV, possibly depending on electron energy. Times for a strictly thermal desorption process, one without electron irradiation, are also shown. For the latter case, the ZnSe surface was exposed to excess Se as before at the various substrate temperatures, but without the presence of electron irradiation. After a sufficiently long time interval, the sample was probed with the electron beam to see if a Zn-stable surface had emerged. The surface was then exposed to Se once again to produce a Se-stable surface. The process was repeated for various delay times prior to electron beam exposure to bracket the Se thermal desorption time. The significant difference in activation energy between the two cases, 2.1 eV vs. ~ 1.0 eV indicates a large electron stimulated desorption effect is present.

3.5.2 The Effect of Electron Irradiation during Growth of ZnSe

One possible effect of ESD of Se could be a decrease in growth rate. To investigate this possibility a RHEED bar was used as the substrate. The RHEED beam was defocused to completely illuminate the RHEED bar. This size substrate is used to ensure coincidence of the electron irradiation and the laser probe. By moving the electron beam on and off the sample while monitoring the film thickness evolution, the effect on growth rate could be determined at various substrate temperatures as indicated in Figure 3-6(a) for growth on a (100) surface. While increasing the substrate temperature lowers the growth rate for both Zn- and Se-stable growth, the presence of high-energy electrons leads to a much more pronounced decrease in growth rate at higher temperatures for Zn-stable growth. A similar effect was not observed for Se-stable growth, as shown in Figure 3-6(b), consistent with the belief that the ESD process is primarily affecting Se adatoms.

Farrell *et al.* determined a thermal activation energy of ~ 0.6 eV for the ESD process from 10 keV electrons in ZnSe, considerably lower than our measured value of ~ 1.0 eV at the same energy. This difference in activation energy may be related to the

Figure 3-5 Time intervals required for a Se-stable surface to evolve to a Zn-stable surface at various temperatures, with and without electron irradiation.

Figure 3-6 ZnSe growth rates with and without electron irradiation for (a) Zn-stable (100) growth, (b) Se-stable (100) growth and Zn-stable (211)B growth.

fact that we used (100) oriented substrates off-cut 2° towards the [011] direction. The resulting higher step density may have caused the Se to be more tightly bound to the surface. To further test this idea, we investigated growth of ZnSe on (211)B-oriented GaAs substrates. This orientation does not exhibit differing reconstructions depending on Zn or Se-stable conditions, precluding RHEED desorption studies. However, as illustrated by the data in Figure 3-6(b), there was not a measurable difference in growth rate with and without electron irradiation on the (211)B orientation up to 380°C under Zn-stable conditions, indicating the effects of ESD were much less pronounced for this highly-vicinal orientation.

Farrell *et al.*¹⁵ attribute the ESD process to the generation of holes in ZnSe, which according to Marfaing¹⁹ will affect the more electronegative surface specie, in this case Se. Simpson *et al.*²⁰ argue that this same process is the underlying origin of photon-stimulated effects also observed for above bandgap light illumination during growth. The observations reported here do not contradict this proposed mechanism, but also do not unambiguously resolve the underlying processes. In addition, there is little discussion in the literature on how the ESD process affects point defect formation, which is important for doping of ZnSe.

3.5.3 The Effect of Electron Irradiation during Growth of ZnMgSe

RHEED stripes have also been observed on ZnMgSe grown by MBE started under Se-stable conditions, which should suppress ESD effects. Figure 3-7 illustrates such a stripe imaged using spatial/spectral imaging. The presence of a RHEED stripe in the alloy provides a possible test to see if ESD primarily affects Se. If there are ESD effects for the Group II specie, it would not be expected to be the same magnitude for both Zn and Mg as they have different binding energies. Thus, a compositional change with high-energy electron irradiation would indicate an ESD effect for the group II adatoms.

A series of $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ samples were grown at temperatures ranging from 250 to 400°C with composition, x , ranging from 0 to 0.45. The samples were grown under an initial excess Se flux that was shown to minimize the effects of electron irradiation for ZnSe. RHEED stripes were observed on each sample.

Figure 3-7 (a) Reflectance image of a ZnMgSe layer at a wavelength of 900 nm. (b) Spectral reflectance from the locations indicated by the rectangles.

Spatial/spectral reflectance imaging allowed measurement of the thickness both inside and outside the RHEED stripe on each sample. Typically thickness changes were less than 2%, with the largest measured change around 8%. The magnitude of the thickness changes ranged around 50 to 150 nm for $\sim 2\text{ }\mu\text{m}$ thick epilayers. Since this is an optical measurement, the apparent thickness change could also be due to a change in composition and thus index of refraction. To check this latter point, measurements were made using a surface profilometer that indicated thickness variations of this order, but instrumental resolution limited quantitative comparison. To probe for compositional variation, low temperature photoluminescence measurements were made comparing the RHEED stripes and surrounding area. The resulting spectra were indistinguishable for each sample, presenting strong evidence that no change in composition occurred from electron irradiation. The photoluminescence result is consistent with adsorbed Se being the primary surface specie affected by high-energy electron irradiation.

3.6 Summary

High-energy electron irradiation can affect the growth of compound semiconductors. A significant electron stimulated desorption effect is observed for Se during the growth of ZnSe and ZnMgSe. Although thickness variations are observed for ZnMgSe, composition remains unchanged. While the effects on growth rate can be minimized either by growing under Se-stable conditions or on high index orientations, this may not give the best conditions for all types of structures. Previous work implies electron-hole generation should increase desorption of the most electro-negative species.^{15, 19,20} The primary effect of high-energy electrons is desorption of weakly bound Se. In addition, it is not yet clear how electron irradiation affects point defect formation. Since high-energy electrons can distinctly alter surface reconstruction and surface chemistry, RHEED measurements must be carefully considered on a case-by-case basis so that observations are not misinterpreted.

CHAPTER IV

4. ZnSe:Cl and ZnMgSe:Cl

Chlorine has been shown to be the most promising n-type dopant in ZnSe. Doping is achieved through the use of ZnCl₂ during MBE growth.⁶⁴ ZnCl₂ is preferable to Cl or Cl₂, as it is believed to sublime as ZnCl₂⁶⁵ and does not result in a memory effect from chlorine gas on the growth chamber walls.⁶⁶ Chlorine atoms are shallow donors with an activation energy in the range of 25-31 meV.⁶⁷ Uniform doping carrier concentration levels up to $\sim 2 \times 10^{19} \text{ cm}^{-3}$ can be achieved. A carrier concentration of $3 \times 10^{20} \text{ cm}^{-3}$ was reported for selective doping (similar to delta doping), although these results have not been reproduced.³² To date, the carrier concentration of ZnSe:Cl as measured by the Hall effect has been correlated primarily to the ZnCl₂ source temperature. Hall results by Ferreira *et al.*,³⁹ XRD by Ohkawa *et al.*,⁶⁶ and PL by Hernandez *et al.*⁵⁹ will be compared to data collected in this study. This effort has attempted to unify the varying results presented by multiple groups by distinguishing and better understanding issues related to carrier concentration, compensation, chlorine incorporation and chlorine solubility. This work has progressed in collaboration with theoretical investigations with Dr. Yaxiang Yang, Dr. Leonid Muratov and Dr. Bernard R. Cooper at West Virginia University.

The ternary compound ZnMgSe is of great interest for use as a cladding layer in optical heterostructures, which in conjunction with ZnCdSe layers, can be used to produce unstrained quantum wells.⁶⁸ For Zn_{1-x}Mg_xSe the index of refraction decreases while the energy gap and the lattice constant increase with increasing Mg percentage.⁶⁹ Initial investigations into doping of this ternary compound with ZnCl₂ have been quite disappointing. ZnCl₂ was chosen due to its success as an n-type dopant for ZnSe. The maximum carrier concentration is significantly lower than for ZnSe, and occurs at a significantly lower ZnCl₂ source temperature. It has been suggested that the reason the maximum electron concentration achievable in a ZnMgSe alloy occurs at a lower ZnCl₂ source temperature is a decrease in chlorine solubility.³⁹ Through the use of modeling Yang *et al.*⁷⁰ predicted that it is not a solubility issue, and in fact Cl_{Se} is more soluble in ZnMgSe. While the formation energy of the Cl_{Se} donor and the compensating Cl-V_{Zn} defect both decrease, it appears the change in band gap due to magnesium is the primary

cause of the decrease in the maximum electron concentration. SIMS measurements performed in the current study have confirmed Yang's solubility prediction. Both the prediction and experiment will be discussed further below.

4.1 Modeling Predictions

Modeling by Yang *et al.*⁷⁰ showed that, for Cl-doped ZnSe, the Cl_{Se}-Zn bond length calculated using a 32-atom supercell increases by about 6.7%. Thus, after averaging over all of the bond lengths, these calculations indicate an overall increase in lattice constant change of 2.0% for uncompensated material in this 32-atom supercell. For compensated material, the most likely contributing defects are Zn vacancies.³³ Upon modeling of a Cl_{Se}-V_{Zn} pair in the same 32-atom supercell, it is found that the spacing between the Cl_{Se} and the V_{Zn} site increases over the Zn-Se lattice spacing by about 3%, the V_{Zn}-Se site spacing decreases about 5% and the Cl_{Se}-Zn spacing increases less than 1%. Upon averaging over the various changes in site positions due to the compensating Cl_{Se}-V_{Zn} complex, a significantly smaller change in overall lattice constant would occur compared to the uncompensated case. Compensation requires both an isolated Cl_{Se} (donor) and a Cl_{Se}-V_{Zn} pair (acceptor). Thus, the rate at which the lattice constant increases with increasing Cl would decrease by about half as the material becomes compensated.

According to modeling results,⁷⁰ Mg atoms have no preferential positions in the Zn lattice for ZnMgSe. However, Yang has predicted that the total energy of a 32-atom supercell containing one Cl atom is 0.57 eV less with Mg atoms as nearest neighbors than one where Mg atoms are not nearest neighbors to Cl. Therefore, it is energetically favorable for Mg and Cl to sit as nearest neighbors in the lattice. The formation energies of doping defects (Cl_{Se})¹⁺ and (Cl_{Se})⁰ are lower for Cl substituting into a Mg-Se bond than for substitution into a Zn-Se bond. This indicates that the solubility of chlorine in ZnMgSe should be higher than in ZnSe. The specific predictions concerning lattice constant and Cl solubility were investigated during this thesis work. Also of interest, although not examined in this thesis work, is that the formation energy of the compensating defect (V_{Zn}-Cl_{Se})¹⁻ decreases at a slower rate than the formation energy of Cl_{Se}¹⁺ in ZnMgSe, favoring formation of uncompensated material. However, Yang *et al.*⁷⁰ have shown that the dependence of bandgap on Mg concentration is the

limiting factor for the maximum achievable carrier concentration, dominating this latter effect.

4.2 Experimental Procedures

A series of both uniformly-doped and step-doped ZnSe:Cl layers were grown on undoped semi-insulating (100) GaAs substrates. Chlorine doping was achieved using a standard effusion cell with ZnCl₂ (99.999%, Johnson Matthey) as source material. Growth conditions were kept Se-stable. These layers were grown under conditions which produced chlorine concentrations ranging from 10¹⁷ to 6x10¹⁹ cm⁻³. All growths were started with approximately 0.3 μm of undoped ZnSe before introducing ZnCl₂ into the growing layer. Cl-doped ZnMgSe samples were grown in a similar fashion, but had an additional 0.15 to 0.3 μm of undoped alloy before exposing the growing layer to a ZnCl₂ flux. For uniformly doped samples the thickness of the doped layer was nominally 2 μm. The growth rate was measured *in-situ* using laser interferometry, with the assumption that the introduction of Cl does not affect the index of refraction of ZnSe or Zn_{1-x}Mg_xSe.

RHEED patterns were monitored during growth along the [010] azimuth. Under Zn-stable conditions the c(2x2) surface reconstruction is observed. The Zn/Se ratio was adjusted until the Zn-stable reconstruction vanished for unalloyed material, ensuring Se-stable growth conditions.⁷¹ This ratio typically ranged between 0.75 to 0.5 based on BFM measurements before the growth.

A prediction of Cl incorporation was made based on the standard equation of flux from an effusion cell using vapor pressure data, standard effusion cell geometry and assuming 100% incorporation.^{72,73} This prediction was compared to SIMS results for three samples as shown in Figure 4-1. The primary sample is a step-doped sample (the SIMS profile is shown in section 4.3.1) which was grown to calibrate ZnCl₂ incorporation. The second sample was a uniform, highly doped sample with a chlorine concentration of 6x10¹⁹ cm⁻³. The third comes from a step-alloyed sample grown under a constant Cl flux with a dopant source temperature of 146 °C. The undoped spacing steps had Cl concentrations of 5x10¹⁸ cm⁻³. BFM readings were also taken of the ZnCl₂ source for temperatures ranging between 133 °C and 225 °C. The trend indicated by the SIMS

Figure 4-1 Comparison of SIMS measurement of chlorine incorporation to predictions based on vapor pressure and effusion cell geometry assuming 100% incorporation.

data correlates well with the predicted variation in ZnCl_2 vapor pressure and BFM readings.

Several samples exhibited a phenomenon not clearly understood. The most highly Cl-doped ZnSe visibly degraded under UV light when viewed with the optical microscope. A number of ZnMgSe:Cl samples also degraded as listed in Table 4-1. This degradation was noticed after room temperature Hall measurements were carried out for sample #0121 and degradation could have been a contributing factor to the temperature dependence of its Hall measurements. Additional pieces of the same sample showed a similar degradation after an extended period of time showing that the degradation was not solely resulting from the Hall measurements. This suggests that a surface layer formed either as a result of a surface reaction dependent on the high dopant concentration or from being coated with photoresist when the indium was etched from the back of the substrate.

4.3 Results

4.3.1 Secondary Ion Mass Spectrometry

SIMS measurements were performed using Cs^+ ions to determine the doping concentration profiles of chlorine.⁷⁴ Uniformly doped samples were coated with gold to prevent charging. The SIMS profile shown in Figure 4-2 is the step-doped structure that was previously discussed as the ZnCl_2 incorporation calibration sample. The step-doped structure was grown to determine the rate at which chlorine incorporates into ZnSe for our standard growth conditions. The structure was grown by sequentially opening and closing the chlorine shutter. Each step consisted of Cl-doped ZnSe grown for one hour at different Cl source temperatures, producing Cl-doped regions approximately 0.4 μm thick. The steps were separated by approximately 0.4 μm of undoped ZnSe with the layer finally capped by a similar amount of undoped material. The ZnCl_2 source temperature was only changed when the shutter was closed. The change in measured Cl concentration as a function of source temperature closely tracks the expected change in vapor pressure. Shown schematically with the SIMS profile in Figure 4-2 is the opening and closing positions of the ZnCl_2 shutter with predicted Cl levels based on vapor pressure and geometry as well as the ZnCl_2 source temperatures.

Atoms cm ⁻³	Sample #	T _{Cl}
5.6x10 ¹⁹	ZnSe:Cl 0121	173
~3.5x10 ¹⁹	ZnSe:Cl 0126	166
~5.4x10 ¹⁸	ZnSe:Cl 00139	146
~1x10 ²⁰	ZnMgSe:Cl 0136	146
~1x10 ²⁰	ZnMgSe:Cl 0146	146

Table 4-1 Summary of samples with degraded surfaces.

Figure 4-2 SIMS figure of Cl incorporation in a step-doped ZnSe film. Shown schematically are the expected incorporation profiles (based on flux predictions) and the opening and closing positions of the ZnCl₂ shutter with associated ZnCl₂ oven temperatures.

The chlorine profile measured for each step was reasonably sharp and symmetric, and did not indicate significant signs of diffusion. There may be a slight tendency towards surface segregation, but the evidence is close to the limit of experimental uncertainty. After the shutter was closed the chlorine reverted to background levels. This transition width was on the scale of 1500 Å (or 5×10^{10} atoms/nm) but has been seen to be as narrow as 360 Å for material grown at a higher growth rate.⁶⁶ Such sharpness in the change of the doping concentrations will be highly beneficial to the growth of electrical interfaces.

Yang *et al.*⁷⁰ suggest that chlorine incorporation will increase with increasing Mg concentration. To test this prediction, an alloy-modulated structure was grown under a constant ZnCl_2 flux. The ZnCl_2 oven was fixed at a temperature of 146 °C, which produces a Cl incorporation of $5 \times 10^{18} \text{ cm}^{-3}$ for pure ZnSe. $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ steps were produced with x-values of 0.16, 0.27 and 0.43 by sequentially opening and closing the Mg shutter in one hour intervals. The ZnCl_2 shutter remained open, and thus chlorine-doped ZnSe was grown before, between, and after the steps to serve as a reference. The Mg oven temperature was increased while the shutter was closed. The sample was grown on, and capped with, an undoped 0.35 µm ZnSe buffer layer. A SIMS profile of this sample is displayed in Figure 4-3. The figure shows both the chlorine concentration and the percentage of Mg in the alloy. Magnesium percentages in this sample were determined by SIMS using direct comparison to a ZnMgSe standard whose Mg concentration was determined using XRD. The Cl incorporation returned to nearly the same level for each ZnSe:Cl layer, and exhibited a dramatic increase during the steps where Mg was present. This dramatic increase of over an order of magnitude clearly shows that there is an increase in solubility of Cl for ZnMgSe. The Cl concentration increases by a smaller percentage from step to step possibly because the sample incorporates nearly all of the available Cl. A comparison between the Mg percentage and the Cl incorporated is more clearly shown in Figure 4-4.

As a result of the increased solubility of chlorine in ZnMgSe, the resulting Cl level incorporated for a Mg molar percentage of 0.43 and a ZnCl_2 source temperature of 146 °C, is significantly higher than for ZnSe as shown in Figure 4-5. The increase in Cl incorporation in ZnMgSe over ZnSe shows that incorporation mechanisms are not

Figure 4-3 SIMS of ZnMgSe compositionally stepped sample grown under constant ZnCl₂ flux.

Figure 4-4 Cl incorporated versus Mg molar percentage.

Figure 4-5 Predicted Cl incorporation verses ZnCl_2 oven temperature for $\text{Zn}_{0.57}\text{Mg}_{0.43}\text{Se}$ based on the increase observed for $T_{\text{ZnCl}_2} = 146$ °C.

efficient in ZnSe.

The drastic increase of incorporated Cl is not expected based on previously measured vapor pressures of ZnCl_2 . The sources for this data used methods for measuring vapor pressure similar to the BFM. This suggests that BFM measurements proved at best to be a relative measurement of ZnCl_2 flux, but were found not to be amenable to quantitative interpretation using standard approaches.⁴⁴ The quantitative discrepancy between the BFM measurements and resulting fluxes may have been due to the high energy required to ionize ZnCl_2 . A ZnCl_2 molecule requires 5.3 eV to dissociate into atoms,⁶⁵ compared to 11.8 eV to ionize ZnCl_2 ^{75,76} and 26 eV to dissociate into ions.⁶⁵ The molecules are more likely to dissociate than ionize, reducing the number of ions producing current in the ion gauge. This effectively decreases the sensitivity factor for the molecule. While this could be investigated through simultaneous mass spectrometry and ion gauge measurements it was beyond the scope of this effort.⁷⁷

4.3.2 Electrical Characterization

The results of Hall measurements performed for this study are summarized in Table 4-2. Room temperature Hall was first attempted with indium contacts. However, annealed Hg-In contacts proved necessary to obtain well behaved ohmic behavior. All samples were then measured using annealed Hg-In contacts. The mobility ranged between 200 and 400 $\text{cm}^2 (\text{V s})^{-1}$. Temperature-dependent measurements were then performed on most samples that were not semi-insulating and had contacts with good ohmic behavior. These measurements were performed on all non-degenerate samples. The temperature-dependent carrier concentrations for these samples are shown in Figure 4-6. The lack of temperature-dependence for the most heavily doped samples is consistent with the observation that electrical conduction at these carrier concentrations is degenerate such that the Fermi level should lie within the conduction band. Samples 0123, 0129 and 0130 had low enough dopant concentrations that they exhibited carrier activation. The activation energies were 16, 3 and 6 meV, respectively. Sample 0121 is highly compensated, but appeared to display carrier activation. The carrier concentration data for this sample was analyzed using the charge balance equation,⁷⁸ which indicated a very small activation energy of approximately 2 meV. Comparison of the expected Cl concentration and the Hall carrier concentration indicates that this sample is heavily

[Cl]	Sample #	sample notes	n	Mobility	n/[Cl]	N _d /N _a
Atoms cm ⁻³			e ⁻ cm ⁻³	cm ² /(Vsec)		
5.6x10 ¹⁹	0121	degraded surface	2.0x10 ¹⁷	200	0.003	1.0
~5x10 ¹⁹	01131	grown Zn-stable	4.4x10 ¹⁸	146	0.088	1.1
~3.5x10 ¹⁹	0126		3.5x10 ¹⁸	160	0.300	1.2
~2x10 ¹⁹	01133	grown Zn-stable	7.9x10 ¹⁸	210	0.395	2.3
~1.8x10 ¹⁹	00132		9.5x10 ¹⁸	210	0.527	2.1
~5.4x10 ¹⁸	00139	non Ohmic degraded surface				
~5.4x10 ¹⁸	0122		3.5x10 ¹⁸	285	0.648	2.8
2.0x10 ¹⁸	00131		1.8x10 ¹⁸	290	0.900	19
2.0x10 ¹⁸	0117		1.1x10 ¹⁸	270	0.550	2.2
~4.5x10 ¹⁷	0129	grown Zn-stable	2.4x10 ¹⁷	400	0.533	3.3
~4.5x10 ¹⁷	0130	T _{sub} 250	2.3x10 ¹⁷	380	0.511	3.1
2.3x10 ¹⁷	0123		6.3x10 ¹⁶	410	0.273	1.8
undoped	01106		2.8x10 ¹⁴	310		

Table 4-2 Electrical characterization summary of Cl-doped ZnSe samples at room temperature measured with annealed mercury-indium contacts.

Figure 4-6 Temperature-dependent Hall measurements on a number of ZnSe:Cl samples. The chlorine concentration is indicated (in cm^{-3}) next to the sample number. Note that samples 0126 and 0121 are highly compensated.

compensated and may no longer show degenerate conduction. For compensating samples it can be difficult to accurately interpret the Hall results. The surface degradation of this sample may also be a contributing factor to its temperature dependence. The rest of the conducting samples with Cl concentrations above $1 \times 10^{18} \text{ cm}^{-3}$ did not exhibit temperature dependence indicating that these layers are fully degenerate.

Electrical characterization results of chlorine-doped layers have typically been reported as a function of ZnCl_2 source temperature. This makes comparison of studies from different laboratories difficult since the amount of incident chlorine for each sample, in addition to being dependent on source temperature, is highly dependent on system configuration, growth rate and other factors. It is often more useful to compare electrical or optical properties to Cl concentration. In order to make such comparisons to data collected by other groups, their Hall data was correlated to chlorine concentration by assuming the sample with the lowest Cl concentration was uncompensated. Then, by assuming a similar incorporation rate for a given flux, our concentration versus ZnCl_2 source temperature calibration was used to “compare” results from other groups to ours. Using this methodology a comparison was made with data from Ferreira *et al.*,³⁹ and is shown in Figure 4-7. This procedure may introduce uncertainties of a factor of 2 to 3 if some amount of compensation is present in their samples, and indeed seems to underestimate Cl concentration at the maximum carrier concentration. A line was drawn to indicate a 1:1 correlation between electron concentration and chlorine concentration. Uncompensated material correlates well with this line because all of the carriers are activated. Above a peak carrier concentration of approximately $1 \times 10^{19} \text{ cm}^{-3}$ for uniformly doped samples the formation of electrically compensating centers, most likely to be $(\text{V}_{\text{Zn}}\text{-Cl}_{\text{Se}})^+$ becomes significant and results in the decline of the carrier concentration seen with increasing chlorine concentration.

Hall measurements of ZnMgSe samples grown in this study were not conclusive. For our growth experiments, we were not yet fully aware of the magnitude of the increased incorporation. The samples thus had much higher chlorine concentrations than anticipated, which resulted in the growth of compensated samples. Annealed Hg-In contacts were required to provide ohmic contacts to ZnMgSe:Cl . All sample results are shown in Figure 4-7 and are summarized in Table 4-3. Data from Ferreira *et al.*³⁹ for

Figure 4-7 Electron concentrations as a function of Cl incorporation for ZnSe and ZnMgSe at room temperature. Note that Ferreira *et al.*'s³⁹ data has been scaled assuming 100% activation for the lowest doped sample, introducing significant uncertainty. The ZnMgSe from Ferreira *et al.* has also been scaled to include the increased Cl incorporation expected for ZnMgSe.

[Cl]	Sample #	Mg	n	Mobility	n/[Cl]
Atoms cm ⁻³		%	cm ⁻³	cm ² /(V sec)	
~1.14x10 ²⁰	0173	26	5x10 ¹⁷	360	0.004
~1.03x10 ²⁰	0150	20	1.8x10 ¹⁸	200	0.017
~5.40x10 ¹⁹	0139	8	2.5x10 ¹⁸	270	0.043
~4.16x10 ¹⁹	0141	6	1.0x10 ¹⁸	310	0.024
~3.28x10 ¹⁹	0136	4	2.0x10 ¹⁸	280	0.074

Table 4-3 Electrical characteristics of ZnMgSe:Cl at room temperature measured with annealed mercury-indium contacts.

$\text{Zn}_{0.64}\text{Mg}_{0.36}\text{Se}$ is also included, as it contains both uncompensated and compensated samples. Note that the results from Ferriera *et al.* were scaled assuming we have correctly extrapolated the ZnCl_2 flux from their ZnSe data and by using the increased incorporation we have measured for ZnMgSe. As shown in Figure 4-7, the rapid decrease in carrier concentration with increasing Cl incorporation due to compensation occurs at a similar Cl concentration in both ZnSe and ZnMgSe. This effect was completely masked when carrier concentration was plotted versus oven temperature.

4.3.3 X-Ray Diffraction

Ohkawa *et al.*⁶⁶ indicated a dramatic increase in lattice constant with increasing Cl concentration for uncompensated material. A Vegard's law extrapolation for Ohkawa *et al.*'s data would give a 5% change in lattice constant for a 1/32 molar fraction of Cl, corresponding to 1 out of 32 atoms. This is indicated in Figure 4-8. The extrapolation does not take into account the strain effects inherent in their thin films, which they indicated by measuring a series of samples grown with different thicknesses. As shown in Figure 4-9, their undoped samples are not fully relaxed but are under compressive strain. In contrast, our undoped layers appear to be thick enough to be relaxed, as suggested by comparison with the reference ZnSe lattice constant.⁷⁹ The experimental lattice constants found for our ZnSe:Cl samples also showed an increase in lattice constant for increasing Cl concentration. Note that the two heaviest doped samples reported by Ohkawa *et al.* are consistent with our trend, suggesting the added chlorine alleviates the strain inherent in the undoped layers. The extrapolation using Vegard's law for our data would suggest an in-plane lattice constant of 7.15 Å for zincblende ZnCl. This results in a 1.6% change in lattice constant for a 1/32 molar fraction Cl-doped sample. These extrapolations are compared in Figure 4-8. The modeling prediction implies that for more highly compensated samples the slope obtained using Vegard's law would be approximately one-half that expected for uncompensated material. Our extrapolation is heavily weighted by compensated material, and is shown in Figure 4-9 to be consistent with the prediction by Yang *et al.*⁷⁰ Both the modeling and experimental Vegard's law extrapolations imply an increase in the lattice constant for both uncompensated and compensated Cl-doped ZnSe with a smaller increase for compensated material.

Figure 4-8 Using a Vegard's Law extrapolation for a 1/32 molar fraction, with Ohkawa *et al.*'s⁶⁶ data, a lattice constant of 5.95 Å was found. Our experimental data extrapolated to 5.71 Å, while modeling predictions by Yang *et al.*⁷⁰ for compensated and uncompensated material were ~5.72 Å and 5.78 Å respectively.

Figure 4-9 Expanded view of experimental lattice constant measurements comparing results from this work to that of Ohkawa *et al.*⁶⁶ The lattice constant of unstrained ZnSe was taken from ref. 79.

It was not possible to investigate changes in lattice constant in $\text{Zn}_{1-x}\text{Mg}_x\text{Se}:\text{Cl}$ samples via XRD because of the lattice constant dependence on the Mg molar percentage in the alloy. XRD is used to measure the Mg concentration, and the small changes due to chlorine incorporation are not distinguishable from variations due to alloying.

4.3.4 Photoluminescence

Chlorine concentrations have been correlated to deep-level luminescence and are related to native defects.⁵⁹ The donor acceptor pair (DAP) recombination is the origin of the 2.1 eV band, where the donor is $\text{Cl}_{\text{Se}}^{1+}$ and the acceptor is a $(\text{V}_{\text{Zn}}-\text{Cl}_{\text{Se}})^{1-}$ complex which is referred to as the Cl A center. This luminescence band is more commonly referred to as a self-activated (SA) luminescence band.⁸⁰ An increase in DAP emission of ZnSe films has been found as a function of Cl doping. The ratio between the edge emission intensity and the DAP peak intensity has been recognized as a method for quantifying increasing compensation through the use of PL.⁶⁶ The excitonic emission occurs around 2.8 eV. Hernandez *et al.*⁵⁹ did not observe any DAP luminescence for concentrations up to $9.4 \times 10^{17} \text{ cm}^{-3}$, whereas for their most highly doped film they did not see the excitonic emission. They have also stated that the DAP band shape is due to interference in the thin films.

Ke Feng performed photoluminescence on chlorine-doped samples in Professor Giles' laboratory. Photoluminescence results are summarized in Table 4-4. Using a bandgap energy of 2.822 eV for ZnSe, and with the (D^0, X) transition occurring at 2.796 eV, the Cl donor ionization energy is 26.2 meV, consistent with prior optical measurements.⁸¹ For the doping levels investigated in this study the donor bound exciton emission has already become the dominant feature. The intensity of this transition is largest near the lower end of the concentration range investigated for these samples. The asymmetric broadening of this emission is ascribed to the Stark effect from charged impurities in bound excitons.^{66,82} In addition, the emission could also be enhanced due to contributions from two-electron transitions. The oscillations are due to thin-film interference. The free exciton line (E_x) at 2.802 eV does not appear for any of these samples reflecting the significant shallow donor concentration. In Figure 4-10 a comparison is made between three samples. The decreasing edge to DAP ratio with

[Cl]	Sample number	n	Edge Emission peak energy	Intensity of Edge Emission	Intensity of 2 eV DAP band	Ratio (edge /DAP) emission
Cl cm ⁻³		cm ⁻³	D°,X (eV)			
5.6x10 ¹⁹	0121	2x10 ¹⁷				
~3.5x10 ¹⁹	0126	6x10 ¹⁸	2.80	less than 100	26664	
~1.8x10 ¹⁹	00132	9.5x10 ¹⁸	2.803	4629	1.4x10 ⁵	0.03
~5.4x10 ¹⁸	00139	non Ohmic	degraded			
~5.4x10 ¹⁸	0122	3.5x10 ¹⁸	2.801	0.39x10 ⁶	10890	36
2.0x10 ¹⁸	00131	1.8x10 ¹⁸	2.796	0.66x10 ⁶	10585	62
2.0x10 ¹⁸	0117	1.1x10 ¹⁸	2.796	1.09x10 ⁶	6812	160
~4.5x10 ¹⁷	0129	2.7x10 ¹⁷	2.796	1.74x10 ⁶	3162	550
~4.5x10 ¹⁷	0130	2.3x10 ¹⁷	2.796	1.25x10 ⁶	1978	632
2.3x10 ¹⁷	0123	2.4x10 ¹⁷	2.796	1.41x10 ⁶	843	1673

Table 4-4 Photoluminescence data of Cl-doped ZnSe.

Figure 4-10 Photoluminescence of ZnSe:Cl. [Cl] is indicated on each plot.

increasing Cl concentration can easily be seen, as well as the DAP band shape. Phonon replicas probably do contribute to the broadening of this peak, but the zero-phonon line cannot be resolved.

For higher chlorine concentrations the (D^0,X) emission energy shifts to a higher energy by as much as 5 meV as shown in Figure 4-11. The shift is highly visible for higher doping concentrations. This shift can be attributed to a decrease of ionization energy of excitons resulting from screening of nearby donor electrons on the excitons.⁶⁶ Hanamura⁸³ has treated this shift in terms of dipole-monopole interactions, while Woodbury⁸⁴ used a non-degenerate fit using Hall results. While both theories were examined neither agreed in a satisfactory manner with the experimental data. This is likely due to both the degenerate nature of the heavy doping and the high degree of compensation.

It was possible to discern DAP emission for all doped samples, but the excitonic emission was almost eliminated for the most highly doped films. By displaying a number of scans for samples with a wide range of Cl concentrations as is shown in Figure 4-12 it is possible to recognize the magnitude of the change in this ratio. Additionally, the shift in the edge emission is also seen for the highest doped sample. It can be seen that as the compensation increases the edge emission decreases significantly.

4.4 Kinetics and Surface Chemistry Effects Observed via Growth Rate

Measurement

The model developed by Yang *et al.*⁷⁰ indicates a maximum carrier concentration will be reached where it is equally likely to create either a donor or a compensating defect. Thus, the carrier concentration should then remain constant for increasing Cl concentration. However, what is observed is a dramatic decrease in carrier concentration with increasing Cl-flux above the maximum attainable carrier concentration indicating an additional driving force for compensation is present. The growth rate was monitored by laser interferometry for samples with a nominal growth rate of $\sim 0.33 \mu\text{m}/\text{hour}$ for undoped ZnSe layers. A decrease in growth rate was observed to occur starting at the ZnCl_2 flux that results in compensated material as seen in Figure 4-13. Chlorine concentration levels above 10^{19} cm^{-3} produced an initial gradual decrease in growth rate,

Figure 4-11 Photoluminescence of edge emission for a range of chlorine concentrations.

Figure 4-12 Peak intensities for DAP and edge emission in 4K PL spectra of ZnSe layers plotted as a function of chlorine concentration.

Figure 4-13 Correlation between decrease in growth rate and carrier concentration.
 ZnCl_2 source temperature is included as a reference.

with drastic effects for concentrations above 10^{20} cm^{-3} , and a complete halt in growth for fluxes expected to give chlorine concentration above $4 \times 10^{20} \text{ cm}^{-3}$. For conditions giving rise to the largest decrease in growth rate, the RHEED images became spotty, and the intensity decreased, indicating a change from two-dimensional to three-dimensional growth. Such surface roughening could result from a competing surface etching process from the impinging ZnCl_2 .

Additionally, as shown in Figure 4-14 the chlorine concentration at which the growth rate begins to decrease is relatively close to where a decrease in the intensity of the PL edge emission occurs. This implies that the growth rate decrease may be an indicator for loss of opto-electrical quality in the growing film.

There has been an effect noted in ZnSe:Cl grown by atmospheric metal organic chemical vapor deposition indicating higher zinc partial pressures depressed the formation of zinc vacancy complexes increasing the highest achievable carrier concentration for this growth method.⁸⁵ Also, in a study by Satoh *et al.*⁸⁶ for samples doped with Cl and heat treated in Zn or Se vapor or in molten Zn, the concentration of isolated Cl_{Se} donors decreased for increasing Se pressure.

In this study the effects of the Zn/Se flux ratio on growth rate were investigated in multiple growth runs to determine if this effect was specific to the growth method. To begin the growth, the Zn/Se flux ratio where the growth is just Se-stable was found using the surface reconstruction, as observed by RHEED, with a BEP ratio of ~ 0.75 . The ZnCl_2 source temperature was then increased until a decrease in growth rate was obtained. Then the zinc source temperature was increased until the original growth rate was achieved. This process of increasing the ZnCl_2 and Zn source temperatures was repeated until the original growth rate could no longer be recovered. Two separate growth runs showing the results of this process are compared to the original growth conditions in Figure 4-15 with lines drawn to aid the eye in following the growth progression. So, if the decrease in growth rate is a direct observation of growth of compensated material, this shows that it may be possible to grow uniformly-doped material with a carrier concentration up to $6 \times 10^{19} \text{ cm}^{-3}$ by increasing the Zn/Se BEP ratio past 1. The growth rate could not be recovered at the highest ZnCl_2 flux. A limited number of observations were made to see if the decrease in growth rate would be

Figure 4-14 Correlation between decrease in growth rate and edge emission. ZnCl_2 source temperature is included as a reference.

Figure 4-15 Effects of Zn/Se ratio on etching effects of ZnCl_2 . ZnCl_2 source temperature is included as a reference.

suppressed though electron irradiation or by growth on a higher index (211)B substrate orientation. These are similar to the investigations described in Chapter III, but these factors did not result in suppression of the decrease in growth rate.

4.5 Summary

Comparison of Cl incorporation using SIMS data from ZnSe and ZnMgSe implies that the incorporation mechanisms for Cl in ZnSe are inefficient, but that with increasing Mg in $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ the incorporation efficiency increases in agreement with modeling. SIMS showed chlorine incorporation profiles that were reasonably sharp and symmetric, but indicate that Cl may exhibit a slight tendency towards surface segregation. Hall measurements found that samples with carrier concentrations above 10^{18} cm^{-3} are degenerate. Samples below this concentration showed carrier activation with activation energies below that of the optically determined value. The carrier concentration followed the same decreasing trend with increasing Cl concentration for both ZnSe and ZnMgSe, suggesting the same mechanism is responsible for compensation in both ZnSe:Cl and ZnMgSe:Cl. Modeling predicts a one to one incorporation of donors to compensating defects, which should result in a leveling off of the carrier concentration, so additional sources of increased compensation are occurring. Electrical and optical characteristics from this study were comparable to those found by other research groups. The experimental Vegard's law extrapolation agrees with modeling, showing an increase in the lattice constant for both uncompensated and compensated Cl-doped ZnSe with a smaller increase for compensated material. Degradation of crystal quality is seen during growth, as the RHEED becomes spotty at concentrations above 10^{20} cm^{-3} .

The free exciton line does not appear for any of these samples reflecting the significant shallow donor concentration even for low dopant concentrations. Photoluminescence of ZnSe:Cl with low Cl concentrations exhibited a strong excitonic peak. With increasing Cl concentration, the excitonic peak decreased in intensity while the DAP peak, which is associated with the Zn vacancy, increased in intensity. The donor bound exciton shifts to higher energies due to a decrease of the binding energy of the excitons resulting from screening of nearby donor electrons on the excitons as the donor concentration increases. The peak also broadens asymmetrically due to the Stark effect from charged impurities in bound excitons. The DAP band shape is most likely

due to thin films interference and phonon replicas probably contribute to the broadening of this peak, but the zero-phonon line cannot be resolved. Samples with higher quality have a higher ratio between the excitonic emission and donor-acceptor pair emission intensities.

A decrease in growth rate occurs when compensated material is grown. For conditions giving rise to the largest growth rate decreases, the RHEED images became spotty, and the intensity decreased, indicating a change from two-dimensional to three-dimensional growth. Such surface roughening could be due to a competing surface etching process from the impinging ZnCl_2 . By increasing the incident Zn flux it was possible to recover the growth rate for an extra order of magnitude of expected chlorine incorporation. The drop off in growth rate and a drop in the PL edge emission are seen at about the same Cl concentration, implying the growth rate decrease may be an indicator for loss of opto-electrical quality in the growing film.

CHAPTER V

5. ZnSe:Cr

Previous incorporation of chromium into ZnSe has focused on bulk crystals through either adding chromium to the melt¹¹ or post-growth isothermal diffusion⁸⁷. These samples allowed for easy spectroscopic and lasing experiments. The use of epitaxial growth techniques would allow fabrication of complex heterostructures that may have advantages for certain applications. As an example, growth of ZnSe:Cr on GaAs should allow for production of integrated structures, opening the possibility of integrated pump and waveguide lasers in the same package. Results are presented that indicate MBE is a viable approach for incorporating optically active Cr in the ZnSe host matrix at levels up to $\sim 10^{19} \text{ cm}^{-3}$ in epitaxial layers, comparable to that achieved for bulk techniques.

5.1 Experimental Procedures

A series of both uniformly-doped and step-doped ZnSe:Cr layers were grown on undoped semi-insulating (100) GaAs substrates. Elemental Cr source material (99.998%, ESPI Ashland, OR USA) was used for doping. Growth conditions were kept Se-stable to minimize site competition and allow for a maximum incorporation of Cr, as Cr enters substitutionally onto the Zn lattice site. These layers had chromium concentrations ranging from 10^{15} to $4 \times 10^{20} \text{ cm}^{-3}$. All growths were started with approximately 0.3 μm of undoped ZnSe before introducing Cr into the growing layer. For uniformly doped layers the thickness of the doped layer was nominally 2 μm . Growth rate was measured *in-situ* using laser interferometry, with the assumption that Cr does not affect the index of refraction of ZnSe.

RHEED patterns were monitored during growth along the [010] azimuth. Under Zn-stable conditions a zinc stable $c(2 \times 2)$ surface reconstruction is observed. The Zn/Se ratio was adjusted until the Zn-stable reconstruction along this azimuth vanished, ensuring selenium stable growth conditions.⁷¹ This ratio typically ranged between 0.75 to 0.5 based on BFM measurements before the growth.

SIMS was performed to determine doping concentration profiles of chromium using O_2^+ ions.⁷⁴ A 2- μm thick ZnSe sample was implanted with a known amount of

chromium to serve as a calibration standard for SIMS analysis. XRD measurements were performed using a Si single crystal monochromator with Cu K α_1 radiation. Lattice constants were determined using the Bond method.⁴⁸ Electrical measurements were attempted with both indium and mercury-indium contacts. All samples proved semi-insulating, which is consistent with Cr substituting into Zn sites, and not acting as an electrically active defect.

Near bandedge PL measurements were performed using above band gap excitation (325 nm at 0.6 Wcm⁻²) and IRPL was performed using below-bandgap excitation of 514.5 nm at 14 Wcm⁻² and 442 nm at 0.35 Wcm⁻² as discussed in Chapter 2.

5.2 Results

5.2.1 Reflection High-Energy Electron Diffraction

RHEED measurements during the growth of undoped ZnSe produced sharp, streaky patterns indicative of high quality layer-by-layer growth, as shown in Figure 5-1(a). With the introduction of chromium to the growth flux the RHEED pattern brightened and the sharp Kikuchi lines intensified. For chromium concentrations up to 3×10^{19} cm⁻³ the patterns remained bright and streaky throughout the growth, as shown in Figure 5-1(b), which indicates Cr does not degrade crystal quality at these levels. At a Cr flux which results in a concentration of 10^{20} cm⁻³ the RHEED pattern becomes more diffuse throughout the growth as shown in Figure 5-1(c). For incorporation at levels above 10^{20} cm⁻³ the RHEED pattern becomes spotty and eventually so diffuse it is no longer discernable, which indicates that Cr at these levels leads to structural degradation.

5.2.2 Growth Rate

The growth rate was monitored by laser interferometry with a nominal growth rate of ~ 0.33 $\mu\text{m}/\text{hour}$ for undoped ZnSe layers. An increase in growth rate was observed upon introduction of Cr as seen in Figure 5-2. Cr concentration levels of 10^{17} cm⁻³ produced a modest 6% increase in growth rate while for a chromium concentration of 4×10^{20} cm⁻³ an increase of 25 to 35% was observed. Considering that this latter amount of chromium only accounts for approximately 2% of the additional material in the crystal

Figure 5-1 RHEED of (a) undoped ZnSe, (b) ZnSe:Cr with a Cr concentration of $3 \times 10^{19} \text{ cm}^{-3}$ and (c) ZnSe:Cr with a Cr concentration of 10^{20} cm^{-3} .

Figure 5-2 Effect of Cr on growth rate.

the chromium must be altering the surface chemistry during growth. Evidence is presented below suggesting surface segregation of chromium is occurring during growth.

One possible explanation for this increase in growth rate comes from considering the constituents of the Se flux. The flux from a thermal source consists of a mixture of dimers, tetramers and higher order species. Thus it is conceivable a Cr rich surface may enhance the “cracking” of the Se molecules, thereby increasing Zn capture and the growth rate.

Another possibility investigated for the increase in growth rate was the possibility of a change in the index of refraction. If this were to occur it would result in a misleading growth rate from the laser interferometry measurements. A number of samples over a range of Cr concentrations had small bars cleaved from the edge to investigate possible cross sectional thickness differences using optical microscopy. For an apparent increase in growth rate of 22% the index of refraction would have to change from $n=2.565$ for ZnSe at 680 nm^{88} to $n=2.118$ to account for the “increased” growth rate. Figure 5-3 compares a sample with a Cr concentration of $3 \times 10^{19}\text{ cm}^{-3}$ to an undoped sample. The cross sections were observed under maximum magnification and there is not a significant difference in sample layer thickness for any of the samples observed. Whereas if the index of refraction did change the thickness of the doped sample would have been 20% thicker than the undoped sample shown in Figure 5-3. The addition of Cr does not have a significant effect on the index of refraction.

5.2.3 Secondary Ion Mass Spectroscopy

A step-doped structure was grown to determine the rate at which chromium incorporates into ZnSe for our standard growth conditions. The structure was grown by sequentially opening and closing the chromium shutter. Each step consisted of Cr-doped ZnSe grown for one hour at different Cr source temperatures, producing Cr-doped regions approximately $0.4\text{ }\mu\text{m}$ thick. The doped steps were separated by approximately $0.4\text{ }\mu\text{m}$ of undoped ZnSe as shown in Figure 5-4(a) with the layer finally capped by a similar amount. The chromium source temperature was changed only when the shutter was closed. The change in measured Cr concentration as a function of source temperature closely tracks the expected change in vapor pressure.

Figure 5-3 Comparison of cross sectional micrographs of a sample with a [Cr] of $3 \times 10^{19} \text{ cm}^{-3}$ and an undoped sample.

Figure 5-4 (a) SIMS measurement of Cr incorporation in a step-doped ZnSe film. Shown schematically are the opening and closing positions of the Cr shutter with associated Cr oven temperatures. (b) SIMS measurement of an uncapped, uniformly-doped ZnSe:Cr film.

A prediction of the chromium concentration was made based on the standard equation of flux from an effusion cell,^{72,73} which relies on the effusion cell geometry and the known vapor pressure of Cr. In addition, BFM readings were also taken with the chromium cell set at 977 °C allowing flux determination based on relative ionization efficiencies.⁸⁹ Additional measurements were not made, as the chromium appeared to be coating the BFM, significantly affecting subsequent BFM measurements. These results are compared in Figure 5-5. The maximum concentrations found by SIMS analysis for each step were within a factor of two of both the prediction and BFM readings. Indeed, the SIMS results were bracketed by the two predictions, suggesting that almost all of the incident chromium atoms are incorporated into the samples.

The Cr profile measured by SIMS is highly asymmetric for each step. The gradual decrease after the shutter is closed is strongly indicative of surface segregation and accumulation of chromium.⁹⁰ At lower Cr flux, as seen for the first step in Figure 5-4(a), the Cr incorporation continues to increase until the shutter is closed, followed by a gradual decrease. For higher source temperatures, the Cr incorporation profile becomes fairly abrupt and constant incorporation profiles are quickly attained. In all cases there is significant Cr accumulation on the surface since Cr continues to incorporate after the shutter is closed. The amount of Cr incorporated after the shutter was closed after the last step (highest concentration) of the step-doped sample was approximately $1.9 \times 10^{13} \text{ cm}^{-3}$ which constitutes ~ 0.025 monolayer of Cr. A uniformly doped sample analyzed by SIMS, with a chromium concentration of 10^{20} cm^{-3} as shown in Figure 5-4(b), also showed evidence of accumulation on the surface. In this sample the doped layer was not capped with an undoped layer. The measured Cr concentration profiles indicate that both the capped step-doped layer and the uncapped uniformly doped layer indicated a surface concentration of Cr.

5.2.4 X-Ray Diffraction

X-ray diffraction was used to investigate the effect of Cr on ZnSe crystal structure. As a result of the lattice mismatch between ZnSe and the GaAs substrate it is possible to distinguish between the diffraction peaks for each material in a θ - 2θ scan.

Figure 5-5 Comparison of actual and predicted Cr incorporation.

This results in a “built-in” GaAs standard. The lattice constants for the film and substrate are then determined from rocking curves. The ZnSe lattice spacing is then renormalized based on a ratio of the accepted value for the GaAs lattice constant of 5.654Å to the lattice constant found from the rocking curve. Lattice constant measurements indicate that Cr has little effect (within $\pm 0.002\text{\AA}$) up to levels of 10^{18} cm^{-3} , while an increase in lattice constant of $\sim 0.005\text{\AA}$ occurred for concentrations of $\sim 3 \times 10^{19}$ and 10^{20} cm^{-3} . Samples with Cr concentrations $\sim 4 \times 10^{20}\text{ cm}^{-3}$ continued this trend, with lattice constants 0.015Å to 0.020Å larger than ZnSe for this concentration as shown in Figure 5-6. XRD full width at half maximums were unchanged within experimental uncertainty for concentrations up to $3 \times 10^{19}\text{ cm}^{-3}$, and indicated structural degradation for higher concentrations. Thus, both XRD and RHEED measurements indicate Cr can be incorporated at levels up to mid- 10^{19} cm^{-3} without structural degradation occurring.

5.2.5 Photoluminescence

Lijun Wang, Ke Feng and Lihua Bai performed photoluminescence on Cr-doped samples in Professor Giles’ laboratory. The near-bandedge PL observed for the undoped and low Cr concentration samples indicated high quality ZnSe, consisting primarily of a combination of free exciton (FX) and donor-bound exciton (DX) transitions as demonstrated in Figure 5-7. The high quality ZnSe was indicated by the observation that FX emission was prominent in many of the samples. With narrower slits, the free and donor bound excitons were resolved and their intensities were compared in Table 5-1. The emission peaks at 2.801 eV and 2.804 eV are due to ground-state free-exciton recombination. The splitting of this peak is most likely due to strain caused by lattice and thermal mismatch. The I_x peak at 2.796 eV and the I_2 peak at 2.798 eV are attributed to radiative recombination of bound excitons at neutral donors.⁶⁶ The main effect on near-edge PL of the incorporation of Cr in the ZnSe layers was suppression of the DX luminescence in most cases, possibly due to site competition. No additional near-edge PL transitions were observed, consistent with Cr not forming electrically active defects. No shift was observed in the FX emission energy for Cr concentrations up to 10^{17} cm^{-3} , consistent with this level of Cr not having a significant effect on either the lattice constant or bandgap. The PL edge emission intensity does begin to decrease for Cr concentrations

Figure 5-6 Lattice constants of ZnSe:Cr for a wide range of Cr concentrations. ZnSe lattice constant is 5.668 Å as taken from ref. 79.

Figure 5-7 High resolution photoluminescence of excitonic emission for ZnSe:Cr are referenced to the right side of the figure. The lower resolution photoluminescence corresponds to the left side of the figure and is shown because these are the intensities reported in Table 5-1.

[Cr]	2.804	2.8004 eV	2.798	2.796	Ratio of F ¹ X/D ⁰ X
	F ¹ X (split)	F ¹ X (split)	D ¹ X	D ⁰ X	
Atoms cm ⁻³	Intensity	Intensity	Intensity	Intensity	
undoped	358	1358	1631	3300	.41
1x10 ¹⁵	322	967	592	928	.33
1x10 ¹⁶	249	894	550	1442	.56
1x10 ¹⁶	304	820	800	775	1.15
1x10 ¹⁷	n/a	120	n/a	96	1.25

Table 5-1 Summary of excitonic photoluminescence, (F¹X) splitting,^{66,91} (D¹X)⁹² and (D⁰X)⁶⁴ for ZnSe:Cr.

greater than 10^{17} cm^{-3} and is completely quenched at levels of $\sim 10^{19} \text{ cm}^{-3}$. Values for relative integrated near-band edge PL intensities are listed in Table 5-1. Since there is not any indication of a significant difference in structural quality over this concentration range, this decrease in emission intensity could be related to the competing absorption pathways introduced by the charge-transfer band of the Cr^{2+} ion. With such strong below-bandgap absorption, it is likely that any radiative recombination due to excitons would be strongly self absorbed in these doped layers.

Infrared PL (IRPL) was observed for many of the samples as shown by the spectrum in Figure 5-8, with emission bands near $1 \mu\text{m}$ and $2.2 \mu\text{m}$. The observed IRPL is very similar to that reported for bulk ZnSe:Cr . The band near $1 \mu\text{m}$ has been observed in diffused bulk ZnSe:Cr to peak at 980 nm with a zero phonon line at 934.6 nm .⁹³ This band has been attributed to both the Cr^{1+} and Cr^{2+} charge states,⁹⁴ so here it is only labeled as being chromium-related. The second band observed at $2.2 \mu\text{m}$ has been assigned to the Cr^{2+} charge state, required for the desired laser transitions.⁹⁴ A summary of all PL results measured over the wide range of doping concentrations are given in Table 5-2. Chromium-related PL was observed from samples with chromium concentrations between 10^{16} and $3 \times 10^{19} \text{ cm}^{-3}$. The 442-nm excitation most likely couples to near-edge transitions of the ZnSe host lattice and excites the Cr-related PL through some charge-transfer mechanism. The 514-nm excitation is more directly coupled through a much weaker absorption band associated with chromium and can be used for the higher concentrations.^{95,96} Above bandgap excitation at 325-nm was also explored for the IRPL, however, only the sample with 10^{18} cm^{-3} Cr exhibited appreciable luminescence. Thus, our results show that below-bandgap excitation at 442nm or 514.5 nm is best to detect Cr-related PL from the thin films. The PL results indicate that optically active Cr^{2+} is incorporated into the MBE layers. The Cr-related PL quenches for Cr concentrations greater than $\sim 10^{20} \text{ cm}^{-3}$, indicating that some mechanism is limiting either the pumping of the Cr^{2+} levels or the levels themselves are quenched. Similar results have been reported for Cr-related IRPL in bulk samples, suggesting the above results are not growth specific.

Figure 5-8 Infrared photoluminescence from ZnSe:Cr.

	442-nm excitation		514-nm excitation		325-nm excitation
[Cr]	1 μm band	2.2 μm band	1 μm band	2.2 μm band	Excitonic PL
Atoms cm^{-3}	Cr related	Cr^{2+}	Cr related	Cr^{2+}	
	Intensity	Intensity	Intensity	Intensity	Intensity
undoped	N.D.	N.D	N.D.	N.D.	2.5×10^6
1×10^{15}	N.D.	N.D	N.D.	N.D.	8.1×10^6
1×10^{16}	2	0.15	N.D.	N.D. ^(a)	1.1×10^6
1×10^{17}	2	0.1	7	N.D.	1.2×10^5
1×10^{18}	72	1.2	16	0.35	1.2×10^3
3×10^{19}	3	0.25	35	0.7 ^(a)	N.D.
3×10^{19}	2	0.15	13	0.4	N.D.
1×10^{20}	N.D.	N.D.	4	N.D.	N.D.
4×10^{20}	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. -none detected

(a additional emission near 1.8 μm)

Table 5-2 Summary of photoluminescence characterization for ZnSe:Cr.

5.2.6 Electron Paramagnetic Resonance

Madelina Chirila performed EPR measurements in Professor Halliburton's laboratory. At best, the EPR results were inconclusive in that no direct evidence of Cr^{2+} or Cr^{1+} was observed. The main feature observed for all samples exhibiting an EPR signal had a g value of 1.998, which is characteristic of chromium exhibiting collective magnetic behavior. A representative spectrum is shown in Figure 5-9. That is, by the time sufficient Cr atoms are present in these relatively thin layers to produce an EPR signal, the Cr spins associated with the d-electrons are interacting and the Cr does not act as an isolated "ion". The small structure shown in Figure 5-9 is not noise, and exhibited a strong orientational dependence. Such behavior is suggestive of magnetic pairing over many sets of Cr atoms. This smaller structure was not seen above a Cr concentration of 10^{20} cm^{-3} , and was too weak to be observed in layers with Cr concentrations below $\sim 10^{19} \text{ cm}^{-3}$. Thus, the EPR signals characteristic of isolated $\text{Cr}^{1+}/\text{Cr}^{2+}$ ions were masked by the collective magnetic behavior observed for these large chromium concentrations.

5.3 Discussion

The observation of Cr-related IRPL indicate both that MBE is a viable method of introducing optically-active Cr into epitaxial layers, and that PL can be used to characterize the Cr in these layers using below bandgap excitation similar to measurements performed on bulk samples.⁹⁵ Of course, the PL results only verify the presence of Cr^{2+} . The next step is to quantify the fraction of Cr in the optically active configuration. We are currently designing experiments to optically pump heteroepitaxial waveguide structures to sample along the length of the structures, allowing a much longer optical path to be investigated.

Of interest, though, is the quenching of the Cr-related IRPL for Cr concentrations above the low 10^{19} cm^{-3} level. If this only occurred for MBE-grown material, one might conclude the quenching is a precursor of the structural degradation that occurs for larger Cr incorporation. However, measurements of Cr-related PL in bulk ZnSe:Cr also show significant quenching above 10^{19} cm^{-3} . In addition, the emission lifetime for Cr in ZnSe has been reported to significantly decrease in bulk ZnSe at similar Cr levels.⁹⁷ Taken together, these facts suggest that there may be a universal phenomenon, occurring at a Cr

Figure 5-9 Electron paramagnetic resonance spectrum for ZnSe:Cr.

concentration of $\sim 10^{19} \text{ cm}^{-3}$, that results in the quenching of the Cr^{2+} levels. The EPR results from this study indicate that Cr at these levels is already exhibiting a collective, magnetic behavior and not acting as isolated Cr. The magnetic interaction is intimately tied to the 3d electrons, which also give rise to the desired optical transitions for lasing. One could speculate that the coupling of the 3d-electrons leading to dilute magnetic semiconductor behavior may also be affecting energy levels needed for Cr^{2+} laser operation. Of course, other mechanisms may be responsible. Further study is required to understand this phenomenon.

5.4 Summary

MBE is a viable route to obtain optically active chromium in ZnSe. XRD and RHEED indicate significant amounts of chromium can be incorporated in ZnSe without significantly degrading crystal quality. SIMS results indicate there is a surface segregation effect. Growth rate changes indicate the presence of chromium changes surface chemistry, increasing the amount of captured Se.

The photoluminescence from epitaxial ZnSe:Cr layers is similar to that obtained from chromium-doped bulk ZnSe, indicating that Cr^{2+} , which is needed for lasing, is present in significant quantities. EPR indicates chromium is acting collectively as a dilute magnetic material at concentrations in the low 10^{19} cm^{-3} . The observation that the optical activity of Cr is quenched at similar Cr concentrations for both bulk and epitaxial ZnSe strongly suggests the limiting mechanism is independent of incorporation technique. More work is required to identify the underlying mechanism.

Chapter VI

6. Conclusions

High quality $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ samples were consistently grown under Se-limited conditions for x concentrations up to 0.40. Sample quality typically degraded for higher Mg percentage, with the exception of a few select samples. The Zn to Mg ratio is difficult to measure in-situ, especially when growing with a II/VI ratio greater than one where the Zn to Mg ratio is difficult to control, but it can be estimated using laser interferometry. Ex-situ the Zn to Mg ratio is successfully determined through XRD and PL measurements.

Electron irradiation during reflection high-energy electron diffraction affects the growth of ZnSe and ZnMgSe by molecular beam epitaxy. The high-energy electrons produce an electron stimulated desorption effect during growth, which primarily affects adsorbed Se. The thermally activated ESD process for Se exhibited an activation energy between 0.8 and 1.0 eV, depending on the energy of the electrons. The fully thermal process had an activation energy of 2.1 eV. Surface reconstructions of a prepared Se-stable surface will evolve from a [011] Se-stable reconstruction into a [010] Zn-stable reconstruction in vacuum. The rate of this evolution increases when the sample is illuminated with high-energy electrons. Electron irradiation also decreases ZnSe growth rates under Zn-stable conditions. The decrease in growth rate can be suppressed by growth under Se-stable conditions. By using (211)B substrate orientations the change in growth rate is also suppressed. These conditions do not necessarily give the best growth conditions for all types of structures. High-energy electron irradiation does not alter composition during the growth of ZnMgSe, but reduces the growth rate through Se desorption as witnessed through thickness changes where RHEED electrons illuminated the sample. It is not yet clear how electron irradiation affects point defect formation. High-energy electrons can distinctly alter surface reconstruction and surface chemistry, therefore RHEED measurements must be carefully considered on a case-by-case basis so that observations are not misinterpreted.

SIMS showed chlorine incorporation profiles that were reasonably sharp and symmetric, but indicate that Cl may exhibit a slight tendency towards surface segregation. ZnSe incorporates Cl at levels up to $2.5 \times 10^{20} \text{ cm}^{-3}$, but is electrically active only to $1 \times 10^{19} \text{ cm}^{-3}$, with compensation occurring beyond this point. ZnMgSe alloys have a higher Cl solubility than ZnSe, increasing the rate of incorporation for increased Mg percentage up to by two orders of magnitude for the same ZnCl_2 flux. Thus, the incorporation mechanism for Cl in ZnSe is shown to be far less efficient than for ZnMgSe. Additionally, the BFM readings, which were in close agreement with reported vapor pressure values, were shown to be inaccurate for determining the total amount of Cl flux available for incorporation into the ZnMgSe samples.

A maximum n-type carrier concentration of $1 \times 10^{19} \text{ cm}^{-3}$ was achieved for ZnSe. Hall measurements showed that ZnSe samples with carrier concentrations above 10^{18} cm^{-3} are degenerate. Samples below this concentration showed carrier activation with activation energies below that of the optically determined value of 26 meV. All ZnMgSe samples grown for this study were degenerate. Due to the increase of bandgap for ZnMgSe, the carrier concentrations obtained for alloyed samples failed to surpass the results of ZnSe. The carrier concentration followed the same downward trend with increasing Cl concentration for both ZnSe and ZnMgSe, indicating the same mechanism is responsible for compensation in both ZnSe:Cl and ZnMgSe:Cl. Modeling predicts a one to one incorporation of donors to compensating defects, which should result in a leveling off of the carrier concentration. There is compensation occurring in addition to the expected one to one incorporation of Cl_{Se} to $\text{V}_{\text{Zn}}\text{-Cl}_{\text{Se}}$.

ZnSe:Cl samples exhibited an increase in lattice constant for increasing Cl concentration. The Vegard's law extrapolation of experimental data agrees with modeling, showing an increase in the lattice constant up to $\sim 0.001 \text{ \AA}$ for uncompensated and up to $\sim 0.003 \text{ \AA}$ for compensated Cl-doped ZnSe grown Se-stable with a shallower increasing trend for compensated material. It is not possible to investigate changes in lattice constant in ZnMgSe due to Cl because of the lattice constant dependence on the Mg molar percentage of the alloy. Degradation of crystal quality is seen during growth, as the RHEED measurements indicate a transition to three dimensional growth at concentrations above 10^{20} cm^{-3} .

The free exciton line does not appear for any of these samples reflecting the significant shallow donor concentration even for low dopant concentrations in the samples. Photoluminescence of ZnSe:Cl with low Cl concentrations exhibited a strong bound-excitonic peak. With increasing Cl concentration, the bound-excitonic peak decreased in intensity while the DAP peak, which is associated with the Zn vacancy, increased in intensity. Samples with higher quality have a higher ratio between the excitonic emission and donor-acceptor pair emission intensities. The largest ratio found for this set of ZnSe:Cl samples was 1673 for a Cl concentration of $2.3 \times 10^{17} \text{ cm}^{-3}$. The donor bound exciton shifts to higher energies by as much as 5 meV. This is due to a decrease of the binding energy of the excitons resulting from screening of nearby donor electrons on the excitons as the donor concentration increases. The peak also broadens asymmetrically due to the Stark effect from charged impurities in bound excitons. The DAP band shape is most likely due to thin films interference and phonon replicas probably contribute to the broadening of this peak, but the zero-phonon line cannot be resolved.

By comparison of the maximum achievable carrier concentration of $\sim 2 \times 10^{19} \text{ cm}^{-3}$ to the Cl concentration in ZnSe found by SIMS it was possible to determine the Cl concentrations for samples from other groups. Electrical and optical characteristics from this study were comparable to those found by other research groups for similar Cl concentrations.

A decrease in growth rate occurs when compensated material is grown. For conditions giving rise to the largest growth rate decreases, the RHEED images became spotty, and the RHEED image intensity decreased, indicating a change from two-dimensional to three-dimensional growth. Such surface roughening could be due to a competing surface etching process from the impinging ZnCl_2 . By increasing the incident Zn flux it was possible to recover the initial growth rate for an extra order of magnitude of expected chlorine incorporation. The drop off in growth rate and a drop in the PL edge emission are seen at about the same Cl concentration, implying the growth rate decrease may be an indicator for loss of opto-electrical quality in the growing film.

Chromium was incorporated in MBE grown ZnSe at concentrations between 10^{15} and $4 \times 10^{20} \text{ cm}^{-3}$. Secondary ion mass spectroscopy concentration profiles strongly suggest that surface segregation and accumulation of Cr occurs during growth. For a Cr step with a concentration of $6 \times 10^{18} \text{ cm}^{-3}$, the amount of Cr incorporated after the step was approximately $1.9 \times 10^{13} \text{ cm}^{-3}$, or ~ 0.025 monolayers.

Growth rate changes indicates the presence of chromium alters surface chemistry, increasing the amount of captured Se. For the highest concentrations the growth rate increased by as much as 35%. Cr may be enhancing the dissociation of higher order Se species increasing the Zn capture and thus the growth rate.

X-ray diffraction and reflection high-energy electron diffraction indicate high structural quality is maintained for Cr incorporation at levels up to $\sim 10^{19} \text{ cm}^{-3}$. Above this concentration XRD peaks indicate the presence of structural degradation. For a Cr concentration of $\sim 4 \times 10^{20} \text{ cm}^{-3}$, the lattice constant was $0.015 \text{ \AA}$ to $0.020 \text{ \AA}$ greater than that measured for ZnSe. EPR indicates that Cr atoms are acting collectively as a dilute magnetic material at concentrations in the low 10^{19} cm^{-3} .

The photoluminescence from epitaxial ZnSe:Cr layers is similar to that obtained from chromium-doped bulk ZnSe. PL indicates Cr is incorporated in the optically active Cr^{2+} state up to levels of $\sim 10^{19} \text{ cm}^{-3}$. Peaks are resolvable in the excitonic emission for ground-state free-exciton emission at 2.801 eV and 2.804 eV, and at 2.796 eV and 2.798 eV due to radiative recombination of bound excitons at neutral donors. The edge emission decreases in intensity for Cr concentrations above 10^{17} cm^{-3} and is quenched for concentrations above $\sim 10^{19} \text{ cm}^{-3}$. Two IRPL emission bands are observed at $1 \text{ }\mu\text{m}$ and $2.2 \text{ }\mu\text{m}$. The $2.2 \text{ }\mu\text{m}$ band is due to the Cr^{2+} charge state while the $1 \text{ }\mu\text{m}$ band is definitely Cr related. The Cr-related PL quenches for concentrations greater than 10^{20} cm^{-3} . The observation that the optical activity of Cr is quenched at similar Cr concentrations for both bulk and epitaxial ZnSe strongly suggests the limiting mechanism is independent of incorporation technique. MBE is a viable route to obtain optically active chromium in ZnSe.

Future work

Investigation and a better understanding of the influences of the Zn to Mg ratio on laser interferometry measurements grown under Se-limited conditions is needed.

Additional PL investigations of RHEED illuminated growths are needed to determine if electron irradiation has an effect on point defect generation. Growth and electrical characterization of uniformly doped Zn-stable samples, grown such that the growth rate does not decrease with the addition of Cl, may confirm a shift of the maximum achievable carrier concentration.

Further attempts should be made to determine the factors contributing to surface degradation of some highly Cl-doped ZnSe and ZnMgSe samples.

Further investigation of Zn-stable and Se-stable growth parameter influences on optical properties of Cr-doped samples will be performed. Optimization of ZnSe:Cr at large Cr concentrations by optimizing growth conditions and quantifying the level of active Cr^{2+} incorporation in ZnSe is also an important step in continuing research. This optimized ZnSe:Cr can then be used first to investigate absorption by total internal reflection of a ZnSe:Cr-ZnMgSe heterostructure. Then, pumping of a $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ Cr-doped active layer with an IR laser will be attempted with an optically-pumped waveguide confinement structure grown with lattice-matched low-index of refraction $\text{Zn}_{1-x}\text{Mg}_x\text{Se}$ cladding layers on either side of the active layer, all grown on a GaAs substrate. Such heterostructures should confine the radiation emitted by Cr^{2+} resulting in a reduced lasing threshold and increased overall efficiency in comparison to homostructures.

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