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Photoluminescence of nitrogen-doped zinc selenide by photo-assisted MOCVD

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Rice University, 1993
RICE UNIVERSITY

PHOTOLUMINESCENCE OF NITROGEN-DOPED ZINC SELENIDE BY PHOTO-ASSISTED MOCVD

by

PAUL MATTHEW GILLESPIE

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE DOCTOR OF PHILOSOPHY

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Abstract

Photoluminescence of Nitrogen-Doped Zinc Selenide by Photo-Assisted MOCVD

by

Paul Matthew Gillespie

Zinc selenide is a wide band-gap (2.67 eV) II-VI compound semiconductor with potential use as a blue electro-optic device material. Problems with obtaining suitable p-type conductivity have limited device development. Zinc selenide epitaxial films, doped with nitrogen from NH₃, have been grown on gallium arsenide substrates by laser-assisted metal organic chemical vapor deposition (MOCVD). The effect of nitrogen doping was investigated with and without direct surface irradiation incident on the surface from a broad-band light source. Low temperature (8 K) photoluminescence spectroscopy has confirmed the incorporation of nitrogen as a shallow acceptor by the presence of acceptor-bound-excitons and associated donor-acceptor-pair recombination emissions. The MOCVD growth parameters have been optimized based on the presence of characteristic features in the photoluminescence spectra.

Growth rate mechanisms have been proposed for both laser-assisted MOCVD and direct-irradiation MOCVD. Simultaneous interaction of the two photo-assisted techniques show that direct irradiation of the surface does not enhance the growth rate under the laser-assisted condition. This confirms that direct surface irradiation
growth mechanisms involve the interaction of photo-generated carriers with alkyl groups from the precursors.
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Chapter 1

Introduction

Zinc selenide (ZnSe) is a II-VI compound semiconductor with a direct band gap of 2.67 eV at room temperature. Wide band gap II-IV semiconductors are receiving increasing attention as possible electrooptic devices in the blue - green range of the optical spectrum\(^1\). The motivation for this work is to develop efficient blue light emitters such as blue light emitting diodes (LED's) and blue solid state lasers. Current LED technology utilizes a combination of gallium arsenide and gallium phosphide doped with nitrogen to make devices which emit from red to green. Direct band gap limitations of gallium phosphide prevent further increases in the spectrum to the blue region. New wide band gap II-VI semiconductors such as ZnSe show promise in attaining devices which emit in the blue. These devices have potential use in flat panel displays, printers, optical data storage systems with improved storage density, and underwater communications. The strong nonlinear properties of these polar materials can also be exploited for unique optical devices as well\(^2,3\). ZnSe also has potential applications as the gate insulator on GaAs MISFETS\(^4\). It has been shown that the interface state density between the ZnSe epilayer and the GaAs substrate (0.27 % mismatch) can be exceptionally low\(^5,6\). These unique optical and electrical properties make ZnSe a material of particular importance and interest.

Epitaxial growth techniques allow material to be produced with few defects and controllable properties, necessary for device applications. Very high quality ZnSe has been produced by molecular
beam epitaxy (MBE)\(^7\)-\(^10\). However, in order to achieve economic production of devices such as blue light emitting diodes (LED's), a process with much more throughput such as metal-organic chemical vapor deposition (MOCVD) would be desirable. Much effort is already underway in this area \(^11\)-\(^18\).

One major problem associated with the development of ZnSe and other II-IV compound semiconductor materials is the control of extrinsic carriers. These can arise from chemically different atoms (impurities) or crystalline defects. Impurities can be present intrinsically (such as a zinc atom on a selenium site), intentionally added to control the doping, or unwanted atoms in the source material. The wide-band-gap II-VI compounds often take on one carrier type when prepared “undoped”. ZnSe is invariably n-type. Doping to enhance the natural carrier type is easily achieved. ZnSe can be doped with Al or Cl to form highly conductive n-type material \(^19\)-\(^21\). Doping to achieve high quality p-type has thus far been difficult. Problems of doping many of the wide band gap semiconductors has been attributed either to “self compensation” and/or equilibrium solubility limits which reduces the incorporation of dopants. Self compensation is a process related to compensating defects becoming energetically favorable after a certain density of impurities has been incorporated into the lattice. Thermodynamic analysis of II-VI semiconductors performed by Neumark et al has shown that the bipolar conductivity may be fundamentally limited by the equilibrium solubility limits \(^22\).

Much effort has been made in trying to make strongly p-type ZnSe. Park et al have doped MBE grown ZnSe with nitrogen by introducing N\(_2\)
or NH$_3$ into the growth chamber. They observed an increase in the photoluminescence (PL) emission attributed to the donor-acceptor D-A transition which was associated with the presence of nitrogen in the films. Nishizawa$^{21}$, using a temperature difference under controlled vapor pressure was able to demonstrate p-type ZnSe growth under limited conditions with carrier concentrations of $10^{15}$ and hole mobilities of around 100 cm$^2$/V-s. Yasuda et al were able to introduce lithium into MOCVD grown material and achieve carrier concentrations in the few $10^{17}$ range, but saw very low carrier mobilities. Stucheli and Bucher$^{24}$ using an iodine transport method reported p-type material with $3 \times 10^{18}$ donors and room temperature mobilities of around 100 cm$^2$/V-s.

Yoshikawa$^{25,26}$ incorporated nitrogen into MOCVD grown material and observed strong D-A emission in the PL spectrum which was attributed to the presence of a shallow nitrogen acceptor level. As the nitrogen incorporation was increased, strong emission from deep centers was also observed, indicating that the presence of defects in the films. Yodo$^{27}$ used ion implantation techniques to put both Li and Na into MOCVD grown ZnSe epilayers. After proper annealing procedures, D-A PL lines were observed which led to the conclusion of p-type material. The resistance of the films was quite high however, and no electrical characterization was reported. Li-doped ZnSe grown by Cheng et al$^{28,29}$ using MBE techniques showed p-type conduction with carrier concentrations of about $8 \times 10^{16}$ and hole mobilities of a few 10's cm$^2$/V-cm.

More recently, Taike et al$^{30}$, achieved reasonable p-type conductivity by doping ZnSe in a metal organic MBE process (MOMBE).
Although they had hole concentrations approaching $10^{18}$, mobilities were still only around 10 cm$^2$/V-s or so, and the PL spectra of the films grown under conditions where the hole concentrations was high ($T_{sub}\text{>400°C}$) were completely dominated by broad mid-band emission showing very poor crystalline quality in the film. In a later paper$^{31}$, these same authors reported a p-n junction formed with MOMBE grown ZnSe. Although SIMS measurements indicated about $10^{19}$ atoms/cm$^3$ of nitrogen were incorporated into the films, only about 0.1% of those were electrically active, resulting in a hole concentration of $5 \times 10^{16}$ and a hole mobility of $\sim 20$ cm$^2$/V-s. The diode did exhibit p-n junction electrical properties however, and some weak blue emission was observed. Because of the presence of a large self-activated (SA) band which peaked around 500 nm the emission from the diode was broad, extending from 400nm to beyond 700nm.

The first blue-green laser diode fabricated from wide-band-gap II-VI semiconductors was reported by researchers at The 3M Company$^{31}$. The devices emitted coherent light at 490 nm from a ZnSe-based single quantum well structure, grown by MBE, under pulsed current injection at 77 K. The p-type ZnSe layers were doped with N from an rf plasma source using N$_2$. Net acceptor concentrations as high as $1 \times 10^{18}$ cm$^{-3}$ were reported.

Significant progress has been made in the past few years in the epitaxial growth of ZnSe, however, p-type doping is still a problem. The limit of the density of free holes is still around $10^{16}$ cm$^{-3}$ by MOCVD and $10^{18}$ cm$^{-3}$ by MBE either because of compensating defects or
equilibrium solubility limits. New techniques must therefore be investigated to try and improve this for future device applications.

This thesis investigates p-type doping of ZnSe with nitrogen from ammonia (NH₃) by two different photo-assisted MOCVD techniques. Photo assisted MOCVD has been a successful technique for lowering the growth temperature of both III-V and II-VI semiconductors. Significant improvements in the electroluminescence properties of MOCVD grown ZnSₓSe₁₋ₓ epilayers has been observed as the growth temperature is decreased ³¹b. Lower growth temperature decreases the number of crystalline defects such as vacancies which may reduce "self compensation" effects.

"Laser assisted" MOCVD employs an ArF excimer laser (193 nm) to photodissociate metal-alkyl chemical bonds rather than thermal energy. The metal alkyl sources, dimethylzinc and diethylselenide, have peak cross sections of absorption near 193 nm and are easily photodissociated. NH₃ also has a peak cross section of absorption near 193 nm ³².

Direct photo assisted MOCVD is another MOCVD technique in which non-equilibrium growth conditions can be obtained by irradiation of the surface with above band gap light. The equilibrium concentration of free carriers in the conduction band is altered which may i) create free electrons and free holes at the surface which can react with organic radical fragments, ii) enhance surface mobility, iii) modify surface bonds, iv) convert surface molecules into atoms, or v) modify electrical potential of the surface ³³. Growth rate enhancement has been observed for ZnSe directly irradiated with above band gap light in MOCVD by Fujita ³⁴.
This thesis investigates the optical photoluminescence properties of N-doped ZnSe by looking at effects of NH$_3$ mass flow rates, non-equilibrium direct irradiation intensity, and laser effects. Growth rate mechanisms are proposed to explain the photo assisted growth processes. Chapter 2 gives a brief review of background semiconductor physics concerning bonding, band theory, carriers, and p-n junctions. Chapter three discusses epitaxial thin films by MOCVD and some of the growth mechanisms and chemistry. It also gives a description of photo-assisted epitaxy and the photochemical reactions involved. Chapter four describes the experimental apparatus of the MOCVD system and describes the experimental procedure of the growth process. Chapter five discusses characterization of thin film ZnSe by photoluminescence spectroscopy and the experimental details. Chapter contains the results, conclusions, and a discussion of the chemical reaction mechanisms important for photo assisted MOCVD.
CHAPTER 2

Background

In order to truly understand the properties of semiconductors and how processing may influence them, it is important to start with some of the basic physics of semiconductors. By considering the atomic arrangement of the lattice atoms and the interaction of electron orbitals, we can better understand optical and electrical properties of the bulk material. By modeling the periodic potential of the lattice atoms, an understanding of the energy band nature of semiconductors can be obtained which yields insight into the nature of electrical carriers, the role of impurities and the interaction of light with these materials. This understanding of the behavior of semiconductors can then be applied to the fabrication of useful electrical devices.

2.1. Bonding in Semiconductors

Semiconductors are crystalline in nature and consist of a periodic structural array of atoms. The interaction of the electrons in neighboring atoms serves to hold the crystal together. The discrete energy levels of an isolated atom are spread into bands of energies as the interatomic distance decreases because the wave functions of electrons in neighboring atoms overlap and the electron is no longer localized at a particular value. The three main types of bonding in solids are ionic,
covalent and metallic bonding. Bonding in semiconductors is usually a mixture between covalent and ionic.

Ionic bonding occurs in many crystals such as alkali-halides. In NaCl, for example, each Na atom is surrounded by 6 Cl atoms and vice-versa. Each atom would like to have 8 atoms in its outer shell (p$_6$s$_2$). Na sodium (Z=11) has a [Ne]3s$^1$ structure and Chlorine Cl (Z= 17) has a [Ne]3s$^2$3p$^5$ structure. Thus Na has one electron in its outer shell while Cl has seven. If the Na gives its one electron to the Cl atom it becomes Na$^+$ with a positive charge and forms Cl$^-$ with a negative charge. Each atom now has a full outer electron shell. The resultant electrostatic force pulls the ions together until a balance is reached by the repulsive forces of the inner shell electrons. All the electrons are tightly bound to the atoms and there are no loosely bound electrons to participate in current flow. Thus ionic crystals are usually good insulators. Ionic bonding occurs for atoms with larger differences in electronegativity (ie. larger separation on the periodic table).

Covalent bonding arises from a quantum mechanical interaction between electrons which are shared between atoms. In diamond lattice semiconductors such as germanium or silicon each atom is surrounded by four nearest neighbors each with four electrons in its outer shell as shown in figure 1 on the next page.
Each electron pair constitutes a covalent bond and the electrons do not belong to a specific atom. As in the case of ionic crystals, there are no free electrons for conductivity. However, an electron may be thermally or optically excited out of a covalent bond to participate in conduction. This is an important property of semiconductors.

Many III-V and II-VI compound semiconductors such as gallium arsenide (GaAs) and zinc selenide (ZnSe) have lattices (diamond cubic) which have two types of atoms and have mixed bonding in which covalent and ionic bonding forces participate. Because the net number of outer shell electrons in a III-V or II-VI pair of atoms is eight, a periodic arrangement can be formed with a sharing of electrons covalently bonding the crystal together. Because the different atoms have differing electronegativities, the bonding is also to some degree ionic. The ionic character of the bond depends on magnitude of the difference in electronegativity of the two atoms. A schematic of the diamond cubic structure of zinc selenide is shown in figure 2.
2.2. Properties of Semiconductors

In solids, electrons take on a range of allowed energy values giving rise to energy bands. There are also regions of energy which are not allowed, known as the band gap or "forbidden band". This can be shown mathematically by modeling the crystal as a periodic potential and examining the allowed energy values which the electrons may occupy. The upper, nearly empty, band is referred to as the conduction band. Because there are many unoccupied states, electrons in this band can participate in conduction. The lower band is referred to as the valence band and contains more tightly bound electrons. Any empty states in this nearly full band act as positive charge carriers called holes. The separation between the top of the valence band and the bottom of the conduction band is known as the band gap. At 0 K semiconductors
have a filled valence band and an empty conduction band as shown in figure 3.

![Diagram of a semiconductor band structure]

Figure 3. Band diagram of a semiconductor at 0 K.

In calculating semiconductor properties and analyzing device behavior, it is often necessary to know the number of charge carriers per cm\(^{-3}\). Electrons obey the Pauli exclusion principal which means that no two electrons may occupy the exact energy and spin state. The Fermi-Dirac distribution function \(f(E)\) gives the probability that an available energy state \(E\) will be occupied at a given temperature \(T(K)\).

\[
f(E) = \frac{1}{1 + e^{(E-E_f)/kT}}
\]

where \(E_f\) is the Fermi energy and \(k\) is Boltzmann's constant (\(8.63 \times 10^{-5}\) eV K\(^{-1}\)). This gives rise to a Fermi level in the energy band gap. The Fermi energy is the energy at which the probability of occupancy is 1/2. At 0 K all energy states below the Fermi level are occupied. The number of charge carriers can be determined by
\[ n = \int f(E)N(E) \, dE \]

where \( N(E) \, dE \) is the density of states (cm\(^{-3}\)) in the energy increment \( dE \).

There are two classes of semiconductor band gaps: direct and indirect. Direct band semiconductors have a minimum in the conduction band and a maximum in the valence band at \( k=0 \). In a direct semiconductor an electron in the conduction band can fall to an empty state in the valence band giving off the energy difference \( E_g \) as a photon of light. An electron in the conduction band of an indirect semiconductor must undergo a change in momentum to a defect state \( (E_l) \) within the band before undergoing a transition. Figure 4 is a representation of electron-hole recombination in direct and indirect semiconductors.

![Diagram of direct and indirect band gaps](image)

**Figure 4.** Direct and Indirect band gaps.
In indirect semiconductors the minimum band separation occurs only with a change in momentum of the electron in an energy vs momentum (E vs k) diagram. Si is an indirect semiconductor while GaAs and ZnSe are direct.

2.3. Charge Carriers

When a semiconductor is heated above 0 K some electrons will receive enough thermal energy to be excited across the band gap from the valence band to the conduction band. The result is an electron available for conduction in the conduction band as well as an unoccupied state in the valence band or "hole". Both the electron and the hole in the "electron-hole pair (EHP)" contribute to conduction.

An intrinsic semiconductor is a perfect crystal with no impurities or lattice defects. It has no charge carriers in the conduction band at 0° K. If EHP's are being created, the number of electrons n equals the number of holes p and at steady state the EHP generation rate equals the recombination rate. The product of n times p is called $n^2$, the intrinsic carrier concentration, and is given by $n^2 = N_c N_v e^{-\frac{E_g}{kT}}$. Here, $N_c$ and $N_v$ are called the effective mass density of states, and are characteristics of each particular semiconductor material, but are normally around $10^{19} \text{ cm}^{-3}$.

It is possible to create carriers in semiconductors by purposely introducing impurities into the crystal or "doping". This is the most
common technique for varying the conductivity. Doping gives the material either a predominance of either electron (n-type) or holes (p-type). Thus, the equilibrium concentration of electrons and holes is different and the material is said to be extrinsic.

When an impurity is introduced into a semiconductor it creates an additional energy level within the band gap known as the donor level or acceptor level. For example, when a group V element such as phosphorus is introduced into silicon (group IV) energy levels very near the conduction band is formed which are each filled with an electron at 0 K. Very little thermal energy is required to excite these electrons into the conduction band and at 100 K virtually all of the electrons from the impurity level have been "donated" to the conduction band. The same is true for acceptors such as group III atoms in silicon such as boron but with holes left in the valence band. Figures 5 and figure 6 show electrons which are thermally excited from donor levels to the conduction band and from the valence band to acceptor levels, respectively.

\[ T = 0 \text{ K} \quad \text{and} \quad T = 100 \text{ K} \]

Figure 5. Band diagram of an n-type semiconductor.
Figure 6. Band diagram of a p-type semiconductor.

Semiconductors often contain both donors and acceptors. When this occurs the net resulting concentration of carriers is the difference between the number of donors and acceptors (|Nd - Na|). Even though both carrier types are present they are said to be "compensated". The predominance of donors, for example, makes the material n-type and the Fermi level is therefore in the upper half of the band gap. Since $E_f$ is above the acceptor level $E_a$, this level is essentially filled with electrons.

Figure 7. Compensation of a n-type semiconductor (Nd > Na).

Filling the $E_A$ states occurs at the expense of the donated conduction band electrons. The requirement for "space charge neutrality" is that
\[ p_0 + N_{d^+} = n_0 + N_{a^-}. \]

where \( p_0 \) = equilibrium hole concentration

\( N_{d^+} \) = number of ionized donors

\( n_0 \) = equilibrium electron concentration

\( N_{a^-} \) = number of ionized acceptors.

2.4. Excess Charge Carriers

Most electronic devices work by the creation of charge carriers in excess of the equilibrium values. These carriers can be created by optical excitation, electron bombardment, an applied electric field, or by the injection of carriers across a forward-biased p-n junction. Information about the excess carriers can be examined by studying the electron-hole recombination mechanisms by optical and electrical techniques such as absorption, photoluminescence, and photoconductivity. This thesis is primarily concerned with the photoluminescence properties of zinc selenide. Chapter 5 will give a more thorough explanation of photoluminescence of zinc selenide.

When electron-hole pairs are created in direct band gap semiconductors they can fall to their equilibrium states by the emission of a photon to maintain conservation of energy. For steady state photoexcitation, the recombination of the EHP's occurs at the same rate as the generation and one photon is emitted for each photon absorbed. Direct
recombination is a fast process and the average lifetime of the EHP's in the process is approximately $10^{-8}$ seconds or less. Often defect levels from impurities, lattice defects, etc... in the band gap has a tendency to trap electrons from the conduction band. The events as depicted in figure 8 are as follows:

1) Incoming photon with $h\nu_1 > E_g$ is absorbed creating an EHP.

2) Excited electron gives up energy to the lattice (as heat) by scattering until it is near the bottom of the conduction band.

3) Electron is trapped at impurity level $E_1$ until it can be thermally reexcited to the conduction band.

4) Direct recombination occurs as the electron falls into an empty state in the valence band emitting a photon $h\nu_2 \sim E_g$.

Figure 8. Trapping of excess carriers.
The delay time between the excitation and the recombination depends on the probability of thermal reexcitation from the trap which depends on the energy level of the trap.

Indirect transitions can also occur but only by the transfer of momentum of the electron to the lattice. The events occur via the recombination levels in the band gap. Any impurity or lattice defect can act as a recombination center if it is capable of receiving a carrier of one type and subsequently capturing the opposite carrier type, thereby annihilating the pair. The indirect transition process is shown in figure 9.

![Diagram](image)

Figure 9. Capture process at a recombination level.

1) Hole capture at a filled recombination center.
2) Electron capture at an empty site.

Since the recombination centers are filled at equilibrium (below $E_F$, the first event of the process is hole capture. This is equivalent to an electron falling from the recombination level $E_R$ to the valence band leaving behind an empty state. Hole capture is a non-radiative process transition. The capture lifetime of this process may be longer because
temporary trapping may occur followed by thermal reexcitation before the second step of the process occurs resulting in a delay.

Energy level positions for each recombination trapping center occur at different values for different impurities. Impurities may act as donors or acceptors when ionized. Some impurities introduce multiple levels in the band gap.
CHAPTER 3

Zinc Selenide Thin Films

3.1 Basics of Epitaxy

Semiconductor electronic devices usually require high quality single crystal material. This can sometimes be very difficult to obtain for certain materials. Growth of bulk crystals is often hindered for compound semiconductors because they do not always melt congruently, i.e. the solid is not in equilibrium with the liquid of the same composition. Therefore epitaxial growth is often required. Epitaxial growth is the deposition of one material onto a substrate in such a way that each atom matches up to a substrate atom to form a repeating crystallographic pattern. Homoepitaxy is the deposition of a material onto a substrate of the same material. Heteroepitaxy is the deposition of a material onto a different material as the substrate. For good quality hetero-films the substrate must be very similar in nature to the material being deposited. It must have a very close lattice match and have the same crystal structure symmetry.

There are many epitaxial growth techniques which have been developed including liquid phase epitaxy (LPE), molecular beam epitaxy (MBE), sputtering, vapor phase epitaxy (VPE), etc. Information on each of these can be readily found\textsuperscript{36,37,38,39,40}. This thesis will primarily be concerned with the vapor phase epitaxy of zinc selenide on (100) GaAs substrates by metal organic chemical vapor deposition (MOCVD). MOCVD is so named because the precursor sources are organometallic
in nature. The technique is also often referred to as Organometallic Vapor Phase Epitaxy (OMVPE). The term MOCVD will be used throughout this paper.

Epitaxial growth is the ordered growth of one crystal upon another such that the crystallographic orientations have a defined relationship to each other. It is derived from the Greek language to mean "arrangement on". Epitaxy is now widely used for preparation of thin single crystal layers of semiconductors for device applications and for basic measurements of electrical properties. The two basic criteria for epitaxy to occur are:

1) There must be matching symmetry between the contacting crystal planes of the substrate and the overgrowth.

2) The misfit between parallel lattice rows must be less than a limiting value of about 15%.

The lattice misfit is usually defined as

\[ m = \frac{b-a}{a} \times 100 \text{ percent} \]

where \( b \) = spacing between the rows in the deposited interface.

\( a \) = spacing between the rows in the substrate.

If the symmetry of the two crystals is the same, the misfit is said to be the same in all directions.

The way in which the atoms arrange themselves on the substrate surface depends on the mode of growth. The growth modes are
classified according to the way in which the arriving mobile deposit
atoms arrange themselves and aggregate on the surface of the substrate
surface. The three main modes of growth are

1) Monolayer growth
2) Nucleated growth
3) Nucleation followed by monolayer growth.

Monolayer growth occurs when the deposited atoms are bound
more strongly to the substrate than they are to each other. The atoms
aggregate to form monolayer islands which spread out until an entire
monolayer is formed. The process continues monolayer by monolayer
until a final thickness is reached. Atomic layer epitaxy (ALE) is a layer by
layer growth technique which utilizes this growth mechanism. ALE is a
specific mode of operating OMVPE processes such that the substrate is
alternately exposed to the different source gases. This growth mode
often utilizes a substrate with a stepped or vicinal surface to enhance the
initial nucleation of the first monolayer. This is achieved by cutting the
growth surface of the substrate slightly off axis. For zinc selenide on
gallium arsenide a 2° off axis of the (100) surface towards the (110)
plane is used.

Nucleated growth occurs when mobile deposit atoms aggregate
as small three dimensional crystals which continue to grow in size until
they touch and intergrow to form a continuous film. This mode of growth
occurs when the binding of the deposited atom to each other is stronger
than to the substrate.
The third mode involves the formation of one monolayer followed by subsequent nucleation of three dimensional islands on top.

Heteroepitaxial growth introduces the idea of strained layer epitaxy. There is often a mismatch of lattice parameters as an epitaxial layer begins to grow. The lowest energy state of a monolayer would be the one matching the spacing of the substrate, provided that the misfit is within acceptable limits. The layer will be either in tension or compression depending on the relative lattice parameters of the epilayer and the substrate. Further strained monolayers can the form on top. Such a strained thin film is only stable up to a limiting value of thickness, and above this thickness the lowest energy state would be a layer of natural atomic spacings. Once this critical thickness is reached, irregularities in the planar spacing are necessary to accommodate the changes by the presence or absence of atomic rows known as misfit dislocations. To accommodate a two dimensional planar misfit, a two dimensional network of edge dislocations or an array of misfit dislocations is necessary. This critical thickness has been determined by earlier work of van der Merwe (1963)\textsuperscript{41}. Olson and Ettenburg have derived an approximate expression of the critical thickness $h_c$ as

$$h_c = \frac{50b}{m}$$

where $b = $ edge component of Burgers vector

$m = $ percentage misfit.

The spacing between dislocations is given by
A schematic of the relaxation of a strained epitaxial layer by the formation of an array of misfit dislocations, or periodic arrangement of extra rows of atoms, as the thickness of the film reaches the critical thickness is shown in figure 10.

Figure 10. Misfit dislocation array at the critical thickness ($h_c$) of a heteroepitaxial layer during growth.
In this figure the substrate has a lattice parameter larger than that of the film causing the film below the critical thickness to be in biaxial tension.

3.2. Metal Organic Chemical Vapor Deposition

Metal organic chemical vapor deposition (MOCVD) is an epitaxial growth process which involves the vapor phase transport in the form of metal organic chemical constituents onto a suitable substrate. There are several advantages of MOCVD over other epitaxial growth techniques. It is a relatively inexpensive process which can also be scaled up for high throughput. The reactor involved is relatively simple and does not necessarily require ultra-high vacuum (UHV) conditions. The disadvantages have mainly to do with the precursor reactants. They are quite expensive and difficult to handle. Many precursors are often toxic and pyrophoric, i.e. they spontaneously combust in the presence of oxygen or air. The purity of many of the sources may also limit the quality of the films obtainable.

In MOCVD the precursor reactants must be transported into the growth reactor in a controllable manner. This involves control over the mass flow rates which govern the hydrodynamics of the system. Most metal organic sources come in the form of high-vapor pressure liquids. Often, mass transport of these reactants is achieved by using hydrogen as a carrier gas. Hydrogen of a known mass flow rate is bubbled through the liquid metal organic sources taking with it some of the metal-organic vapor. Calculations regarding this process are shown in chapter 4.
Once the metal-organic sources are in the growth reactor, energy must be supplied to dissociate the metal-organic bond. This is usually achieved simply by thermal energy from the heated substrate but can also be aided by the irradiation of photons of sufficient energy (Laser-Assisted MOCVD). The dissociated species can then deposit stoichiometrically onto the substrate. A schematic of this process for dimethylzinc and diethylselenide is shown in Figure 11.

![Schematic diagram of gas phase species in MOCVD process](image)

Figure 11. Schematic representation of the gas phase species during the growth process of ZnSe using DMZ and DESe. Some of the chemical reactions which may occur are:

\[
(CH_3)_2Zn + H_2 \rightarrow Zn + 2CH_4
\]

\[
(C_2H_5)_2Se + H_2 \rightarrow Se + 2C_2H_6.
\]

Modeling of the MOCVD process is often very difficult. Many of the exact chemical mechanisms are still largely unknown. Most of the growth studies are empirical techniques which give the growth process the general appearance of an art. The typical approach has been to treat it as a "black box", turning knobs until the desired properties are obtained.
However, new techniques are being developed using fast pulse lasers to track the presence of reaction products with time which may help in the understanding of some of the reaction mechanisms.

To understand the growth dynamics, the growth process can be divided into thermodynamic and kinetic components. Thermodynamics determines the driving force for the growth process and kinetics defines the rates at which the process will occur. The hydrodynamics of the reactor control the mass transport of the material to the solid-vapor interface. Each of these factors plays a role in the overall growth process.

The macroscopic study of growth rate of films as a function of different growth parameters can give insight to the growth mechanism. Shaw 42 showed growth rates as a function of substrate temperature allows general categorization of the process limiting the growth as 1) mass transport, 2) surface kinetics, or 3) thermodynamics. Figure 12 shows the dependence of growth rate on substrate temperature for the different growth mechanisms.

![Figure 12](image)

Figure 12. Growth rate dependence on substrate temperature for kinetically limited, mass transport limited and thermodynamically limited mechanisms of growth.
There are also other experiments to determine rate limiting step of the growth process. If substrate orientation effects the growth rate then this is a sign that surface reaction kinetics are limiting the growth. If changing the total velocity of the flow while keeping the partial pressures the same effects the growth then the growth is mass transport limited.

In the case of kinetically limited growth, the overall process can be treated by classical rate theory.

\[
\text{Rate} = A e^{-\frac{Q}{RT}}
\]

\[
\ln \text{Rate} = \ln A - \left(\frac{Q}{RT}\right)
\]

By plotting \(\ln \text{rate versus } \frac{1}{T(K)}\), the activation energy \(Q\) can be determined from the slope. The activation energy \(Q\) is the energy required to overcome the energy barrier in going from the reactants to the products as shown in figure 13.

![Free energy diagram of growth process.](image)

*Figure 13. Free energy diagram of growth process.*
Since $E_1 > E_2$, the reaction is thermodynamically favorable but must first overcome the activation energy barrier $Q$. This activation energy $Q$ can be explained as a summation of all the energetic processes involved in the reactants becoming the film (i.e., breaking bonds, transportation to the surface, surface diffusion, enthalpy of formation, etc.).

This thesis investigates the growth rate dependence on photochemical interactions to yield insight to possible growth mechanisms. 193 nm ArF excimer laser radiation photo dissociates organometallic sources in the gas phase, changing the activation energy of the growth process. Direct surface irradiation with above band gap photons affects chemical reactions which may occur on the surface involving the creation of free electrons. The interaction of these two processes yields information about the growth mechanisms.

3.3. Photo Assisted Growth of Semiconductors

Photochemical processing is an important semiconductor fabrication method. Photo assisted epitaxy is a relatively new approach in the growth of semiconductors which affects the growth process in a controllable manner by enhancing certain photochemical reactions either on the surface or in the vapor phase. It has advantages over conventional processes such as permitting growth at lower temperatures and spatially selective growth control. Lower growth temperatures reduce interface mixing cause by diffusion, solubility of impurities, and the density of crystalline defects. Photo sources include broad band sources such mercury and xenon lamps or monochromatic coherent
laser radiation such as excimer lasers. Photo assisted growth can be separated into 1) gas phase irradiation and 2) surface irradiation. Gas phase irradiation effects the vapor phase reactions above the semiconductor surface particularly in growth processes such as MOCVD. The irradiation may be either perpendicular or parallel to the sample surface. Direct surface irradiation is usually incident perpendicular to the sample surface and primarily affects chemical reactions which occur at the semiconductor surface.

3.3.1. Vapor Phase Irradiation

In growth processes such as MOCVD, large metal organic molecules contain semiconductor source species bonded to organic radicals. The molecules must be chemically dissociated by breaking the bonds of organic radicals from the desired semiconductor source species. This is typically accomplished using thermal energy from the heated substrate. However, higher substrate temperatures increase crystalline defects and impurity incorporation. By using photon energy rather than thermal energy to break the bonds then growth can occur at lower temperatures. Laser-assisted MOCVD has been successful in attaining low temperature growth of both III-V and II-VI compound semiconductors. Significant improvements in the electroluminescent properties of MOCVD grown ZnS$_x$Se$_{1-x}$ epitaxial layers has been observed as the growth temperature is decreased$^{43}$. Photo assisted vapor phase epitaxy requires that the source gases which are to be photo dissociated have a high cross section of
absorption at the photon energy which is used. Most metal alkyls used in MOCVD have a strong broad absorption in the ultraviolet region of the spectrum below 250nm. Broad band mercury or xenon lamps as well as excimer laser radiation at 193nm or 248nm have been used in photo assisted MOCVD. Shinn et al have shown that parallel 193nm irradiation from an ArF excimer laser enhances the growth rate in ZnSe films grown by MOCVD between 200°C-500°C from dimethylzinc and diethylselenide sources \(^{44}\). The sources dimethylzinc and diethylselenide have comparable cross sections of absorption of 1.8X10^{-17} and 1.9X10^{-17} cm\(^2\) respectively at 193nm \(^{45}\) as shown in figure 14.

![Graph showing absorption cross section vs. wavelength](image)

**Figure 14.** Cross sections of absorption for dimethylzinc and diethylselenide.
CdTe $^{46,47,48}$, HgTe $^{46,49}$, Cd$^{1-x}$Hg$^x$Te $^{46,50}$, Si $^{51}$, GaAs $^{52}$, and InP $^{53}$ have all been grown using photo assisted vapor phase epitaxy. Ando et al have demonstrated low temperature MOCVD growth of ZnSe by perpendicular irradiation with a low pressure mercury lamp $^{49}$.

3.3.2. Direct Surface Irradiation

Photo-assisted epitaxy by direct surface irradiation is a relatively new processing technique for semiconductor growth which involves irradiation perpendicular to the sample surface with above band gap photons. Surface irradiation can be used in vapor phase epitaxy as well as in molecular beam epitaxy (MBE). Photochemical reactions at the sample surface enhance certain growth mechanisms. Direct irradiation of the surface during growth is considered a "non-equilibrium" growth technique because the number of free carriers in the sample may be altered by above band gap light. Some of the other effects include $^{55}$:

1) Enhancement of surface mobility of constituent atoms.
2) Modification of surface bonds.
3) Conversion of surface molecules into atoms.
4) Modification of the surface electrical potential by the generation of electron-hole pairs.

Direct irradiation of the surface has been shown by Fujita et al. to greatly increase the growth rate of ZnSe and ZnS in OMVPE $^{56}$. They found that the growth rate increase is not due to thermal effects or gas
phase reaction effects by observing the effect of irradiation both horizontal and vertical to the sample surface 57.

One explanation is that excess carriers from electron-hole pairs which are generated by light absorption promote surface reactions such as elimination of alkyl groups from molecules which are chemisorbed or physisorbed on the surface. By using a broad-band xenon lamp and a series of low-pass filters, they have shown that the growth rate enhancement occurs only for radiation greater than the band gap of the material and less than the photo dissociation energy of the source gases. Fujita has shown constant growth rates 1-2 mm/hr from 500°C -300°C under above band gap irradiation 58. The films however, exhibited bad surface morphology, reduced deep level emissions, and increased residual donors attributed to chlorine from the dimethylzinc processing.

To examine the phenomenon of alkyl group elimination from the surface, Fujita et al. have performed mass spectroscopy of metal alkyls as a function of substrate temperature and photo irradiation wavelength 59. They have shown that diethyl alkyls (C₂H₅ - R - C₂H₅) thermally decompose to form C₄H₁₀, and that dimethyl alkyls (CH₃- R - CH₃) thermally decompose to form CH₄. They have shown that these characteristic species form when the substrate is heated to a temperature of ~400°C or when the substrate is irradiated with photons above the band gap of the deposited material 60.

Direct photo irradiation has also been used in molecular beam epitaxy (MBE). In MBE, a reduction in the growth rate is often attributed to photodesorption of surface ad atoms 61. A mechanism of selective charge transfer has also been proposed.
Direct irradiation has been used in MBE of ZnS$_x$Se$_{1-x}$ using Hg lamp perpendicular irradiation $^{62}$. This work found an increased free exciton intensity in the photoluminescence spectrum of irradiated epilayers, increased sulfur composition, but produced a roughened morphology.

Workers at North Carolina State University have used direct irradiation photo assisted MBE (PAMBE) in the doping of II-VI compound semiconductors $^{63,64,65,66,67,68}$. They have grown highly conductive n-type and p-type CdTe films using In and Sb respectively. The films have shown 100% activation of the dopant sources as determined by SIMS and Hall measurements. The photoluminescence spectra provided evidence of reduced density of point defects and compensating defects. This group has also grown CdMnTe (a dilute magnetic semiconductor), HgCdTe films, and CdMnTe-CdTe quantum well structures and superlattices using this technique.

The mechanism proposed for the high doping levels achieved in these II-VI semiconductors involves preferential photodesorption of one of the constituent species. Reflective high energy electron diffraction (RHEED) studies have shown that surface irradiation from a He-Ne laser increases Te desorption from the CdTe surface. The existence of the vacant Te site favors the incorporation of substitutional acceptors such as Sb$_{Te}$ and As$_{Te}$. 
Chapter 4

Experimental Apparatus

4.1 MOCVD System

Metal organic chemical vapor deposition (MOCVD) is a processing technique for the growth of epitaxial thin film semiconductors. Source atoms of the semiconductor constituents are deposited from the vapor phase in a growth reactor onto a heated substrate. The reactor design and the experimental parameters control the gas dynamics and the growth conditions. The MOCVD system involves a combination of several sub-systems working together. Figure 14 is a schematic of the experimental apparatus used in the laser-assisted MOCVD growth of zinc selenide. The system was designed and constructed by coworkers at Rice University. The major sub-systems which will be discussed include i) gas delivery, ii) metal organic sources, iii) the reactor, iv) exhaust system, v) system control panel, and vi) the excimer laser system.

The system is constructed entirely of stainless steel with welded connections, VCR fittings with silver plated nickle gaskets, or conflat flanges with copper gaskets used at all connections. All stainless steel parts were electropolished or etched in a 5% HF, 10% HNO₃ solution to remove any deposits resulting from the welding and to passivate the surface. Each part was carefully checked with a helium leak detector to 10⁻⁶ torr during assembly.
Figure 15. Schematic of Laser-Assisted MOCVD system.

The entire system is enclosed in a plexiglass enclosure three feet wide by eight feet long by eight feet high supported by a steel Unistrut frame. Two exhaust fans are used to maintain a slightly negative pressure in the event of any leaks which may occur. Hydrogen detectors are placed in the enclosure and in the room.

The control for the system consists of a rack mounted panel which contained a valve sequencer, mass flow controllers, pressure controllers, temperature controllers, and a safety alarm system. Gas cylinders for the
laser-assisted chemical vapor deposition (LAMOCVD) system are located in a ventilated gas bottle cabinet.

4.1.1. Gas Delivery System

Hydrogen is the gas used to transport the metal organic sources during growth. Since very careful control of the purity of gases is necessary in the growth of semiconductors, a hydrogen purification system is employed. Extra dry grade hydrogen is passed through a 0.1μm particle filter, a Johnson-Matthey Inc. OR-50 oxygen remover, a sodium aluminosilicate water remover, and the through a Johnson-Matthey Inc. HP-50-VCR hydrogen purifier. The purifier operates by diffusing hydrogen through a heated palladium barrier.

The mass flow rate of the hydrogen gas is carefully controlled by Unit Instruments Inc. UFC-1000 mass flow controllers. The mass flow rates of the metal-organic sources are controlled by the mass flow rate of hydrogen through constant temperatures bubblers of the sources. The bubbler configuration is shown in Figure 16.

![Diagram](image)

Figure 16. Metal-organic bubbler configuration.
The metal-organic sources are dimethylzinc and diethylselenide. These are high vapor pressure liquids like most metal-organic sources used in MOCVD. A trap prevents the possibility of reverse flow of the metal organic liquid if a pressure reversal should occur. The mass flow rates of these sources can be determined by the temperature dependent partial pressure of the metal organic, the mass flow rate of the hydrogen carrier gas, and the total pressure above the bubbler as shown:

\[ Q_{MO} = Q_{H_2} \times \frac{P_{MO}}{P-P_{MO}} \]

where,

- \( Q_{MO} \) = metal organic flow rate (sccm)
- \( Q_{H_2} \) = hydrogen carrier gas flow rate through the bubbler (sccm)
- \( P \) = total pressure in the bubbler (torr)
- \( P_{MO} \) = vapor pressure of metal organic (torr)

The vapor pressures of the metal organic sources are temperature dependent and can be calculated by the equations (Alpha data)

\[
\log (P_{DMZ}) = 7.802 - 1560/T(K)
\]

\[
\log (P_{DESe}) = 7.905 - 1924/T(K)
\]
The temperature of the metal organic sources is maintained in Brinkman Instruments Lauda RMT - 6 constant temperature baths containing ethylene glycol. The metal-organic sources were purchased from commercial vendors in 100 gram units with VCR fittings and manual shut off valves. The dimethylzinc was purchased from Stauffer Chemical Company Specialty Product Division with a purity of 99.9999%. The diethylselenide was purchased from Alpha Products with 99.995% purity. The sources are highly pyrophoric, meaning they combust spontaneously in the presence of oxygen.

The pressure in the reactor and in the bubblers are measured using a Baratron capacitance manometer (MKS Instruments Inc. model 222CA=01000BB). Pressure control is maintained using automatic feedback controlled pressure controllers (MKS Model 250B and 248A) to throttle valves downstream.

Ultra high purity grade helium can also be introduced into the system to purge out the reactor before and after growth procedures. Electronic grade ammonia gas is used as a nitrogen dopant source in the p-type ZnSe experiments. The mass flow rate is also controlled by a Unit Instruments Inc. 50 sccm. mass flow controller. Ultra-high purity grade nitrogen is used to purge out the ammonia mass flow controller before and after each growth.

4.1.2 LAMOCVD REACTOR

The LAMOCVD reactor is a 304 stainless stainless steel chamber where the growth of zinc selenide occurs. It consists of two concentric
rectangular tubes in which hydrogen and the source gases can flow. Figure 17 is a schematic of the reactor in cross section.

![Schematic of reactor cross section](image)

Figure 17. Schematic cross section of reactor.

The reactor is composed of three sections: i) an inlet, ii) growth region, iii) and an exhaust region. Each section is connected by 6 inch conflat flanges sealed with copper gaskets.

The inlet section is where the gases enter the chamber and are mixed. There are five inlet ports where gases enter radially into a 4.5 inch conflat flange between the bolt holes. The gases enter a volume where they mix and pass through several screens before flowing down the inner tube. The purpose of the fine mesh stainless steel screens is to homogenize the flow and prevent direct streaming. Not all of the five inlets were used but are available for future use.

The outer growth chamber of the reactor consists of a 4 inch by 2 inch by 0.083 inch wall rectangular stainless steel tube 12 inches in length. Inside is a 3 inch by 0.75 inch by 12 inch rectangular stainless steel tube in which the actual source gases flow. To allow for parallel
laser irradiation, window ports are placed on either side. Magnesium fluoride windows epoxyed into 2.75 inch conflat flanges are used because of their high transmission (~92%) at ArF excimer laser wavelength of 193 nm. A 4.5 inch glass viewport is placed on the bottom of the reactor to allow direct perpendicular irradiation of the sample during growth. A 6 inch conflat flange is connected to the top of the reactor from which the substrate holder was attached. A detailed view of the outer chamber is shown in figure 18.

Figure 18. Design of outer growth chamber.
A transverse cross section of the growth region is shown in Figure 19.

![Cross section diagram](image)

**Figure 19.** Cross section of growth region.

Purging of the windows is extremely important in laser processes to prevent deposition on the windows. A two-stage purge scheme is used to prevent this. Hydrogen is introduced at each window to give positive flow away from it and act as a barrier to the metal organic vapors. The laser window is extended 3 inches from the chamber and a baffle the size of the input beam is inserted in the tube connecting the window flange to reduce the cross sectional area and further prevent window deposition. Hydrogen is also introduced between the inner and outer tubes and allowed to flow parallel to the main gas stream. The mass flow rates are adjusted to match the velocities in the two tubes. The two purge schemes are shown in figures 16 and 18. The substrate is mounted up side down on a stainless steel square block which is supported by the
upper 6 inch flange and fitted into a square hole in the top of the inner tube as shown in figure 20.

![Diagram of substrate mounting support](image)

Figure 20. Substrate mounting support.

The up-side-down configuration has two purposes: i) to reduce natural convection effects and ii) to eliminate the problem of dust particles settling on the surface from gas phase nucleation. The substrate holder is attached to the top 6 inch flange by four small (0.030 inch) rigid wires held by set screws. The distance is fixed so that when the 6 inch flange is in place, the substrate holder sits just flush with the top of the inner tube in a fitted hole. The top 6 inch flange supporting the substrate holder is bolted to the top of the outer chamber. This allows very easy removal during sample changes.

The substrate is heated by two 250 watt cylindrical cartridge heaters (2.5 inches long by 0.25 inch diameter) connected in parallel. The temperature is monitored by a type J thermocouple (2 inch long with a 0.063 inch stainless steel sheath) fastened by a set screw on the heater block. The thermocouples were purchased from Omega Inc. with
ceramic mini connectors (PN EI 1103208-SICSS-062U-2 in.). The thermocouple and electrical connections are made with 1.33 inch mini conflat flange vacuum connectors purchased from Ceramaseal Inc. (PN #808B8369-01-CF and #809C10184-02-CF). The substrate holder and all electrical connections are attached to the 6 inch flange on the top of the chamber and can be removed during sample changes without breaking any electrical connections. Temperature control of the substrate holder is maintained by regulation of the voltage to the heaters using a variable transformer. An on-off temperature controller is also

Figure 21. Heater substrate holder.
attached but was not used because of thermal fluctuations greater than 2
degrees Celsius. The GaAs substrate was attached to the substrate
holder by two stainless steel clips on each side. Figure 21 is a schematic
of the substrate holder design.

Pressure is measured and controlled in the chamber by a Baratron
capacitance manometer which is attached to the chamber. Pressure
control is obtained by a pressure control valve on the inlet to the pump.
The valve is controlled by the input from the Baratron in a feedback
controller. Pressure can be controlled in the 0 to 1000 torr region with
accuracy within several tenths of a torr. Calibration is checked with a
thermocouple pressure gauge connected in a tee with the Baratron.

4.1.3 Exhaust System

Flow of the gases in the LAMOCVD system is pumped by a
Leybold Heraus Model D30A Trivac vacuum pump with an ultimate
pressure of 10⁻³ Torr and pumping speed of 760 liters per minute. After
exiting the reactor chamber, the exhaust gases bubble through a trap
filled with silicone diffusion pump oil (Corning D-705, 10⁻¹⁰ Torr) to
prevent any possible backstreaming of air and trap particles formed in
the reactor. An inverse bubbler trap was placed immediately upstream of
this to catch any oil in the event of pressure imbalances.

The exhaust region consists of a rectangular pyramidal shaped
cone to funnel the exhaust gases to the pump with a minimum amount of
turbulence as shown in figure 22.
Figure 22. Exhaust cone.

It consists of a 6 inch conflat flange bases with a 4 inch by 2 inch opening tapering down to a 1 square inch opening in a 2.75 inch conflat flange. The height is 6 inches. The exhaust cone is connected to a 2 inch diameter cross which has connections for the pump and a quadruple mass spectrometer.

A pyrolysis furnace is used to remove unreacted metal-organics and possible toxic by-products before they can be released to the atmosphere. It consists of a clam shell furnace containing a 24 inch long stainless steel tubes with an outer diameter of 1.5 inches. It contains a large surface area of copper turnings inside and is heated to 850 °C. Deposits eventually form inside the tube causing a pressure drop to great to maintain the reactor pressure under flow conditions and the tube periodically has to be replaced. Sometimes it is necessary to run a long pipe cleaner in the 0.5 in tubing connecting the tube to remove additional build up. The gases then pass through a 0.1 μm particle filter.

Hydrogen selenide is a possible by-product of the MOCVD reaction and pyrolysis. The exhaust gases enters an adsorption trap at
the inlet of the mechanical pump. The trap contains potassium hydroxide
impregnated alumina pellets and a layer of activated charcoal. The
caucistic oxidizes the selenium and prevents toxic fumes from being
exhausted to air. The trap also eliminates backstreaming of pump oil into
the reactor system. The remaining hydrogen gas and unreacted
hydrocarbons are the diluted with 8 standard liters per minute of dry
nitrogen to reduce the hydrogen concentration below its explosion limits.

4.1.4 Control Circuitry

The control panel consists of a rack mount panel with modular
units for control of temperature, mass flow rates, pressures, and a valve
sequencer with safety interlocks. The entire LAMOCVD system contains
35 air actuated, normally closed valves. A panel with a schematic of the
system with toggle switches for the valves and LED indicators is used to
open and close valves during growth procedures. The toggle switches
control electrical signals to operate solenoids which allowed air pressure
to actuate the bellows valves. The stainless steel bellows valves require
a pressure of 70 psig to open them. Power to operate the solenoids is
provided by a 35 amp, 12 volt power supply.

During a growth procedure, different configurations of valves are
required to be opened. A panel with a series of preset valve
configurations, determined by switches, can be used to select a particular
sequence of valves. The system can be operated by the preset valve
configurations or in the manual mode with the toggle switches.
Safety interlocks were designed to shut down the process and close all valves upon triggering. System shut down will occur when there was an over pressure in the chamber or either bubbler, detection of combustible gas in the room, or reduction in the pressure of the air supply operating the valves.

4.1.5 Excimer Laser and Optics

An ArF excimer laser (Questek model 2420) is used for these experiments. The laser has a wavelength of 193 nm, power of approximately 200 millijoules per pulse, repetition rate of 50 Hz, and a pulse width of 15 to 20 nanoseconds full width at half maximum. It is a very useful source of ultraviolet radiation. Excimer lasers typically operate with a gas mixture of a rare gas (Ar, Kr, or Xe), a halogen (F or Cl), and helium buffer gas which is excited to higher energy levels by a high voltage discharge. Excited dimers of the halogen and the rare gas are formed and emit ultra-violet radiation during the electronic transition from the excited state to the ground state.

In LAMOCVD, ultraviolet radiation can be used to photodissociate metal-organic molecules during the growth process to lower the activation energy necessary for growth to occur. The ArF excimer laser was chosen in our case because dimethylzinc, diethylselenide, and ammonia all have peak absorption cross sections around 193 nm.

The ArF excimer laser parameters are easily controlled by a microprocessor display panel which uses a quartz beam splitter and detector to continually measure and keep the beam energy constant.
The output of the beam typically decreases with time as impurities form in the gas mixture. The lifetime of the fill is greatly increased with the use of a liquid nitrogen trap gas processor. The cryogenic trap condenses out gas impurities. The "boost" command could also be used on long growth experiments. This continually upgrades the gas fill with use of the microprocessor feedback.

Experiments were done passing the beam parallel to the substrate surface. The beam was directed with the use of two beam steering mirrors and a lens to partially focus it into the volume of gas directly below the substrate. The mirrors were dielectric coated for maximum reflectance at 193 nm radiation at 45° incidence angle. The lens was made of fused silica with a focal length of 25 cm. The beam entered the chamber through a MgF window in a conflat flange with transmission greater than 90% when clean. Energy loss by the mirrors, lens, window, and absorption in air was approximately 50%.

4.2. Procedures of Growth

4.2.1. Substratate Preparation

ZnSe films were deposited epitaxially on GaAs wafers. The GaAs wafers were 2 inches in diameter and grown by the Czochralski technique. They are "semi-insulating" meaning that they are lightly doped with Fe and Cr to act as deep level traps for any free carriers. This gives them a bulk resistivity greater than $10^7$ ohm-cm. Each wafer is
polished on one side and approximately 15 mils thick. The wafers come individually packaged and are “epi-ready”.

The GaAs wafers must be cut into several pieces before they are used as substrates because of the cost of each wafer (about $95). Substrate cleanliness is extremely important in epitaxial growth. Much care is needed when handling the wafers. The wafers are sectioned into four quarters along (100) crystallographic directions. The sectioning is done by cleaving them with a sharp razor blade. The wafer is placed on a hard flat surface with a Kimwipe underneath. Force is carefully applied on the blade onto one of the flats of the wafers at an angle such that a crack is initiated and propagates across the entire wafer as shown in figure 23.

![Diagram of wafer cleaving technique]

Figure 23 Wafer cleaving technique.

This technique is far superior to the traditional wafer scribing technique with a diamond tip scribe. Scribing tends to leave thousands of small GaAs dust particles which could not be entirely removed even with applying pressurized gas and then ultrasonic cleaning. Observations made under an optical microscope at 400 X with a
Nomarski phase contrast attachment reveal that the cleaving technique is orders of magnitude cleaner.

This set of experiments does not involve varying the surface by sample preparation. None of the samples were chemically etched. The samples were simply cleaved, dusted off with "Dust Off Plus™", loaded into the chamber, and thermally heated to 600 °C for 5 minutes in a reducing atmosphere to remove the native oxide.

4.2.2. Growth Procedure

A new substrate was loaded for each growth procedure. This usually involved the removal of a previously grown sample. The overall procedure involved several steps:

1. Post-deposition hydrogen flow until $T_{\text{sub}}$ less than 35 °C.
2. 3 cycles of reactor pump out followed by helium back fills.
3. Opening the reactor.
4. Removal of previous sample, mounting of new substrate.
5. Changing copper gasket and resealing the reactor.
6. 3 cycles of pump out followed by helium back fills.
7. Pre-deposition hydrogen flow - 20 minutes.
8. Thermal etch to remove native oxide 600 °C for 5 minutes.
10. Growth.
The GaAs substrate was fastened to the substrate heater holder by a stainless steel (spring steel) clip on each side. The clips were shaped in such a way that by tightening the screws they would firmly hold the sample flush against the holder. Intimate thermal contact is very important in epitaxial processes to reduce thermal gradients and produce uniform film thickness. The substrate holder would build up deposits with time and would periodically be scraped off with a razor blade. Complete cleaning of stainless steel parts contaminated with selenium compounds can be performed as follows:

1. 5% NaOH, 10% KMnO₄ solution - 1 hour.
2. 5% HF, 10% HNO₃ standard stainless steel etch.

This oxidizes the selenium in aqueous form preventing the formation of H₂Se gas from the acid etch.

Before a growth experiment the reactor would be pumped out and back filled with ultra high purity grade helium three times and hydrogen would flow for 20 minutes to remove any residual oxygen which might be present. GaAs has a native oxide which is removed by heating it up to 600°C for 5 minutes in 100 torr of flowing hydrogen. The temperature was then ramped down and stabilized at the growth temperature. After a growth experiment, hydrogen carrier gas would purge the reactor to remove any unreacted metal organic compounds and also dissipate heat from the sample until it was cool enough to remove.

Safety precautions are necessary any time a sample is being changed or the system is going to be opened. Protective clothing and a respiratory apparatus were used during all steps in which the system was open. A laboratory coat, disposable Tyvec™ sleeves, dustless gloves,
and half mask respirators with cartridge filters were usually worn. In case of more effective safety requirements, full body suits and a full head and face shield with clean air hoses from an auxiliary location could be used. All disposable clothing and used copper gaskets would then be disposed of in sealed metal cans stored under a fume hood which would be labeled for disposal by a hazardous waste service.
Photoluminescence Spectroscopic Characterization

5.1. Introduction

Photoluminescence spectroscopy is a sensitive tool for the investigation of intrinsic and electronic transitions at defects and impurities in semiconductors. Photoluminescence (PL) means luminescence excited by photons. PL detects optical emission as an excited electronic state relaxes to a lower state.

Any imperfection introduced into a perfect crystal causes a disruption of the periodic structure of the lattice and alters the electrical and optical properties of the material. Localized electronic states are produced in the band gap by such imperfections. The location of these states within the band gap largely depends on the ionization energy of the defect. Some of the electronic states are electrically active depending on their relative position in the band gap. Some may be radiative centers while carriers in other states may not relax with a radiative emission. By analyzing the spectrum of the radiative emission, the energy levels of the radiative impurity and defect levels can be determined. This provides information about the quality of the material.

In order to observe these transitions, electrons must be excited to energies greater than the defect level by irradiating the material with photons of energy greater than the band gap. Most spectroscopic studies must be carried out with the sample at very low temperatures to
prevent thermal ionization of optically active centers and to minimize
spectral line broadening by lattice vibrations. Electrons excited into the
conduction band from the valence band thermalize and then recombine
at an active center often yielding a radiative emission of characteristic
energy. The total radiative emission from the sample can then be
optically collected and analyzed with a spectrometer to give the
characteristic photoluminescence spectrum.

5.2. Experimental Apparatus

The experimental arrangement of equipment for
photoluminescence is shown in figure 24.

![Diagram](image)

Figure 24. Photoluminescence experimental set up.

325 nm radiation from a 10 mW Helium-Cadmium laser is the excitation
source. The beam is propagated through a UV grade quartz prism (P1)
to remove visible plasma lines from the He-Cd laser discharge. The
beam is reflected off three dielectric mirrors (m1, m2, m3) to lengthen the
optical path to permit spatial filtering of the plasma lines from the desired
UV radiation. The beam is modulated with a mechanical chopper (C1) to permit phase-sensitive detection (lock-in amplifier) so as to reduce interference from background light. The detector only sees light in phase with the chopper. The excitation beam is tightly focused and directed onto the sample by a lens (L1). The sample is mounted on a copper cold finger of a CTI\textsuperscript{TM} Cryogenics model 22 refrigeration unit with a custom made Janos\textsuperscript{TM} vacuum cryostat. The cryostat is a two stage closed-cycle refrigeration system capable of temperature control down to approximately 8 K. The sample is fastened to the copper block by a few small drops of rubber cement around the edges. The cryostat is evacuated by a mechanical pump to prevent condensation of water vapor in the air onto the sample. The cold finger is surrounded by a highly reflective radiation shield to prevent radiative heat transfer from the outside housing of the cryostat. Holes in the radiation shield allow light to pass freely. Light enters and exits the cryostat through two UV grade fused silica windows epoxied to the housing of the cryostat. The sample is mounted at 45\degree to the incident beam. Luminescence from the sample is emitted in all directions and is collected normal to the sample. The luminescence from the sample is collected and directed onto the spectrometer slit by a lens (L1) of focal length 15 cm. Before the light enters the spectrometer it passes through a low-pass filter (F1) which cuts wavelengths shorter than 375 nm to prevent any scattered 325 nm UV light from the HeCd laser from entering the spectrometer. Neutral density filters (F2) are also often used to reduce the intensity of the luminescence.
The spectrometer is a 0.5 meter Acton Inc. SpectraPro.500™. It has the following gratings:

1) 2400 grooves/mm holographic
2) 1200 g/mm blaze = 500 nm
3) 600 g/mm blaze = 500 nm

The three gratings are mounted on a carrousel and can be chosen via the software. It has slits which are adjustable down to 10 µm and an aperture ratio of f/6.9. The spectrometer is computer controlled by a Texas Instruments Inc. PC through a RS-232 interface. The light is detected with a Hammamatsu Inc. model R943-02 photomultiplier tube (PMT). It has a GaAs photocathode which has a spectral response which is flat throughout the visible spectrum and a very high sensitivity.

The data acquisition is entirely computer controlled. A block diagram schematic of the equipment is shown in figure 25.

![Diagram](image)

Figure 25. PL data acquisition.

The software which runs the data acquisition is a program called "ACTONPL.BAS" written by coworkers at Rice University. It is listed in Appendix II. The program records the sample ID, material, temperature, date, operator, and filename. It lets you choose wavelength range, data
increment, time between data points, and the desired grating. It sets the spectrometer to the beginning wavelength, measures the output from a digital voltmeter readout of the lock-in amplifier signal via IEEE-488 bus, stores the intensity as a voltage, steps to the next wavelength and repeats the process until the spectrum is completed. The program draws the spectrum on the monitor as the data is being taken. The data is stored to disk as a string of intensities preceded by text which tells the starting and finishing wavelength and the data increment. Plots of the spectra are made by an HP 7470A plotter connected to the Texas Instruments PC using a software program called “APLOT.BAS” listed in appendix II. Plots of the spectra are also made using Kaleidagraph on a Macintosh computer.

5.3. Experimental Procedures

Loading a new sample for PL analysis usually involves removal of the previous sample. The vacuum cryostat must be warmed up to at least 285 K before opening it to prevent the condensation of water and ice from moisture in the air. The temperature can be more rapidly increased if desired by back filling the evacuated chamber with dry grade nitrogen and/or turning on the heater of the temperature controller. The heater consists of a resistive nichrome wire wrapped around the base of the cold finger, coated with vacuum epoxy. Care must be taken not to heat it up above 298 K to prevent burning the epoxy. Once the chamber is warmed up and at atmospheric pressure it can be opened up by the handle on the 0-ring retaining clasp.
To remove the sample, the outer housing must be removed and the radiation shield removed using an Allen wrench. The copper cold finger should be removed and placed in a horizontal position to prevent the possibility of the sample falling off during the mounting procedure. The samples are fastened to the copper block using several small drops of rubber cement around the perimeter of the sample to allow easy removal. After the cement has dried, the copper cold finger can be remounted and tightened down. Once the sample is in place the following steps should be taken:

1) Replace the radiation shield with Allen screws.
2) Replace and align cryostat housing using o-ring.
3) Fasten o-ring retaining clasp handle.
4) Evacuate cryostat with mechanical pump to approx 100 mtorr.
5) Turn on compressor for 10 minute warm up.
6) Turn on cold head refrigerator (heater off).
7) Monitor temperature until desired temperature is reached.
8) Turn on He-Cd laser and all electronics for 10 minute warm up.

When the sample is cold and the laser is on, a small blue spot should be visible on the sample in the cryostat. The beam can be directed to the desired location on the sample by lens (L1). The luminescence spot is to be imaged onto the spectrometer slit using lens (L2). A white card is often necessary to help align the light onto the spectrometer slit. The spectrometer should be turned to a wavelength where a PL peak should occur. This can be done by using the program "ACTONPL.BAS" and selecting manual control in the software and then
using the ACTON spectrometer control unit (see manual for details) to tune to the desired wavelength. Once a signal is detected it can be maximized by adjusting the phase of the lock-in and adjusting lens (L2) to optimize the signal. By varying the wavelength on the spectrometer to find the maximum intensity in the spectrum, the lock-in gain settings and NDF filters (F2) can be determined to give a spectrum which is both on scale and has a maximum signal to noise ratio.

Care must be taken in in determining the parameters of the desired spectrum. The resolution of the spectrum is determined by the reciprocal linear dispersion (RLD) of the grating, the spectrometer slit width, and the data increment. The slit width and data increment must be chosen such that no gaps or overlaps occur in the spectrum. For example if a resolution of 0.1 nm is desired and the RLD = 1.5 nm/mm, the data increment should be 0.05 nm and the slit should be set at 33 μm (0.05/1.5). As the desired resolution is increased, less light enters the slit and the signal to noise ratio decreases. The lock-in amplifier must then be set to a more sensitive setting and the time constant must often be increased to reduce fluctuations. Likewise, the time between data points should be increased in the software. Usually a spectrum is taken over the entire visible spectrum with a resolution of 0.5 nm (slit =60 μm, grating = 1200 g/mm) and the over the near band edge with a resolution of 0.01 or 0.02 nm (slit = 10 μm, grating = 2400 g/mm).

5.4. Photoluminescence of Zinc Selenide

Optical spectroscopy is a valuable tool for studying the general properties as well as the quality of ZnSe films. Photoluminescence (PL)
is a useful nondestructive technique for analyzing radiative transitions in semiconductors. There are many types of radiative transitions which may occur in II-VI semiconductors such as zinc selenide. Some of these transitions include the normal band to band recombination of electrons and holes, the recombination of free excitons, bound excitons, free to bound transitions (free electron-acceptor, free hole-donor), and bound to bound transitions (donor-acceptor pair recombinations). A schematic of some of these transitions is shown in figure 26.

Figure 26  Competition of recombination and reemission process:

1) Bound exciton emission.
2) D-A emission.
3) Free electron - bound hole emission.
4) Free electron - deep acceptor.
5) Exciton emission at isoelectronic center.
6) Non-radiative recombination.

In II-VI compound semiconductors such as zinc selenide the ionic nature of the bonding causes the optical properties to be dominated by excitons. A direct radiative band-to-band recombination occur only infrequently. When an electron-hole pair is formed by optical excitation, the hole has to make a choice between:
1) binding to an electron in order to form a free exciton, which has a high cross section because of the long range coulomb potential.

2) binding to a charged defect level (mainly acceptors or double acceptors).

3) binding to a neutral defect level forming a positive charged defect (isoelectronic impurity - small cross section).

The mechanism with the largest cross section will predominate. This is shown schematically in figure 27.

Figure 27. Capture of minority carrier (hole) by:

a) Electrons.

b) Single and double acceptors A-, A--.

c) Isoelectronic center.

The PL spectrum of zinc selenide is dominated by excitonic emissions. Excitons annihilate radiatively with a lifetime of approximately $10^{-9}$ s at 4K 70.
Excitons can exist in the following form:

1) free excitons (FE) - interaction of a free electron and a free hole.

2) bound exciton (BE) - interaction of an exciton and a lattice atom.

Bound excitons may involve donor atoms (donor bound excitons), acceptor atoms (acceptor bound excitons), or neutral atoms.

The binding energy of the free exciton is given by the Rydberg formula

\[ E_x = \frac{m_r q^4}{2\varepsilon^2 e^2 n^2} \quad n=1,2,\ldots \]

\[ m_r = \text{reduced mass} \quad \frac{m^*_n m^*_p}{m^*_n + m^*_p} \]

\[ \varepsilon = \text{dielectric constant of the semiconductor} \]

\[ h = \text{Plank's constant} \]

\[ q = \text{charge of electron.} \]

The binding energy of the lowest energy free exciton is theoretically 25.7 meV. Since an exciton contains both types of carriers, it does not contribute to electrical conduction.

Excitons often couple with phonons (particularly longitudinal optical (LO) phonons) to give repetitions of the free exciton emission in the PL spectra. The emission is found at

\[ h\nu = E_g - E_x - n\varepsilon\omega_{LO} \]

\[ \omega_{LO} = \text{longitudinal optical phonon frequency} \]

\[ E_g = \text{band gap energy.} \]
Typically $\omega_{\text{LO}} = 31.9$ meV in ZnSe. The band gap ($E_g$) increases with decreasing temperature and is 2.83 eV at 4 K. The free exciton emission is often the highest energy emission and is observed at 2.803 eV. Mechanical strain in the films can often lower the observed energy of the emission by several meV.

5.4.1 Free Excitons

The study of the free exciton (FE) transition in ZnSe epilayers represents a powerful tool for obtaining information about the film. It yields information about:

1) the stress situation in heteroepitaxial layers
2) defect concentration
3) the presence of misfit dislocations within the layers

Strain affects the band structure of ZnSe by splitting the upper valence band into light-hole ($E_{1}^{L}$) and heavy-hole ($E_{1}^{H}$) subbands as shown in figure 28.

![Diagram of band structure](image)

Figure 28. Schematic structure of splitting of ZnSe bands due to strain
a) unstrained
b) biaxial tensile stress

ZnSe films grow coherently under strain due to the difference in lattice parameter ($a_{\text{ZnSe}} = 5.6693$ Å, $a_{\text{GaAs}} = 5.6533$ Å) up to a critical thickness of $\sim 0.15$ μm before misfit dislocations form to relieve the stress.

Figure 29 shows a comparison of the near band edge photoluminescence of ZnSe grown on different substrates.

Figure 29. PL of ZnSe grown on different substrates.  

a) ZnSe on GaAs (100).
b) ZnSe on ZnSe (100) wafers.
c) Bulk ZnSe.
Free exciton (FE) luminescence lines are present in both (a) and (b) layers but are missing in the ZnSe bulk grown sample. This indicates better quality and purity of the films compared to the bulk. In bulk ZnSe recombination of free excitons is prevented by fast capture at impurities.

The PL spectrum of (b) a heteroepitaxial film exhibits one free exciton peak \( E_x \) (2.802 eV) (442.49 nm) which has been compared to more pure samples in other experiments showing that no strain exists in homoepitaxial films \(^{75}\). The PL spectrum of a ZnSe/GaAs heterostructure shows two FE features \( E^H_x \) (\(~2.802\) eV) (442.49 nm) and \( E^L_x \) (\(~2.800\) eV) (442.81 nm) characteristic of heteroepitaxial layers as a direct consequence of strain. The very presence of the FE peak in a PL spectrum indicates high quality film.

The energy of the FE emission is higher than that of bound exciton emission. It therefore has a higher cross section of reabsorption and the intensity may be lower than expected \(^{76}\). This is true particularly in thicker layers. In films \(< 1\mu m\) the heavy-hole exciton will dominate while film \(> 1 \mu m\) are dominated by the light-hole exciton.

Misfit dislocations introduced at the interface in order to relax the strained ZnSe lattice not only influence the exciton energy position but also their emission intensities by suppressing their direct radiative recombination. The misfit dislocation concentration is essentially zero for very thin films and increases with layer thickness and reaches a maximum value at about 0.6 \( \mu m \) before it decreases when the layers
grow thick and the lattice sufficiently relaxes. This can be seen in a plot of the ratio of the so-called "Y line" (2.60 eV) (476.87 nm), attributed to defects such as dislocations (described in greater detail in the next section), to the FE line as a function of sample thickness as seen below in figure 30.

![Graph](image)

Figure 30. Plot of the ratio of the intensity of the "Y-line" to the free exciton intensity as a function of film thickness.

Efforts have been made to decrease or eliminate strain at the film-substrate interface by using Zn$_{1-y}$(II)$_y$Se$_{1-x}$(VI)$_x$ alloys on GaAs, GaP, and ZnS$_x$Se$_{1-x}$ layers have been grown by MOVPE and MBE. The PL of these films shows a FE peak much stronger than the BE peak or deep center emission indicating a much lower concentration of non-radiative centers, high purity, and excellent crystalline quality.

ZnSe epilayers (1.4 μm thick) have been removed from the substrates by a suitable selective etch of the GaAs and studied in
transmission. They showed only one FE at 2.8022 eV indicating that the strain has been removed when the ZnSe layer is not in contact with the substrate.

5.4.2 Deep Level Emission (DLE)

One of the first indications of poor film quality is the presence of deep level emission in the photoluminescence spectrum. Deep level emission mostly occurs under non-optimal growth conditions and is related to undesirable defects or impurity levels. DLE is distinguished by the following PL features.

- "Y" line emission at ~ 2.6 eV (476 nm) associated with extending defects such as threading dislocations which can reduce carrier mobility.

- "S" or "M" lines at 2.5 eV (495 nm) often with longitudinal optical (LO) -phonon coupled replicas similar to those seen with donor-acceptor pairs, involving shallow donors and distant deep acceptors of about 275 meV ionization energy.

- broad-band so called "Cu-green" emission centered at about 2.3 to 2.4 eV (516 to 539 nm) attributed to unintentional incorporation of copper during growth. It is often accompanied by \( I_{1}^{\text{Deep}} \) at about 2.78 eV due to the Cu-acceptor-exciton complex or a \( V_{\text{Zn}} \) acceptor site.
- "self activated" (SA) broad band luminescence between 2.14 and 1.97 eV (579.4 to 629.4 nm) related to \( V_{Zn}\) or \( V_{Zn/GaZn} \) complex defect center.

Suppression of DLE and the presence of sharp BE lines is taken as an indication of successful doping without the generation of undesired defects and/or compensating centers. Electrical properties such as the conductivity characteristics of the layers is closely connected to the relative strengths of impurity-related transitions. N-type ZnSe has been prepared with low resistivity but problems in low resistivity p-type ZnSe are generally attributed to acceptor impurities or residual impurity effects.

5.4.3 Bound Excitons

The incorporation of impurities and defects in epitaxial ZnSe gives rise to a number new features in the PL spectrum. Control of intrinsic (like vacancies) and extrinsic (like background impurities) is necessary for the production of precisely intentionally doped and conducting ZnSe. The purity of the ZnSe depends on:

1) growth conditions
2) growth temperature
3) quality of Zn and Se sources
4) choice of substrate material
5) stoichiometric conditions
6) layer thickness.
Intentional doping of ZnSe can possibly be achieved by the following intentional impurities:

**Acceptor dopants**

- Group I elements (Li, Na, or Cu) on a zinc site.
- Group V elements (N, P, or As) on a selenium site.
- Zinc vacancies ($V_{Zn}$) = acceptors.
- Zinc on a selenium site = acceptor.

**Donor dopants**

- Group III elements (Al, Ga, or In) on a zinc site.
- Group VII elements (F, Cl, or I) on a selenium site.
- Selenium vacancies ($V_{Se}$) = donors.
- Selenium on a zinc site = donor.

Purity statements obtained from optical properties can be based on the ratio of FE/BE transition intensity and Deep Level Emission (DLE)/BE intensity ratio.

### 5.4.4 Donor Bound Excitons

Unintentionally doped ZnSe exhibits n-type conductivity regardless of the growth technique. Low temperature PL spectra typically shows two DBE peaks usually labeled I$_2$ and I'$_2$ with a typical
energy separation of about 2 meV. Notation in the literature varies and these lines are also seen as I_x and I_2 or I_{20} and I'_{20}. The origin of these two lines is not clearly determined. The lower energy peak I_2 (typically at 2.795 eV) (443.60 nm) usually dominates and is attributed to native donors, and the upper peak I'_2 (2.7967 eV) (443.33 nm) to substitutional impurity donors \(^{100}\). Other authors assign them to splitting of the "bulk" I_2 lines by stress effects into heavy- and light-hole components \(^{101}\).

The chemical nature of this neutral donor species is also still questioned. Most authors believe it is due to Ga donors on a zinc site caused by out diffusion from the GaAs substrate. I_2 lines have also been attributed to In and Cl impurities \(^{102}\). It is difficult to distinguish binding energy variations due to the exchange of the particular donor center from strain induced variations with respect to the I_2 lines, and because their energies are often very close (in an 1 meV range).

### 5.4.5 Acceptor Bound Excitons

The production of low-resistivity p-type ZnSe is well known to be very difficult. P-type layers have been demonstrated using nitrogen, lithium, phosphorus, and sodium \(^{103}\). The conductivity problems p-type ZnSe have generally been attributed to self-compensation of the acceptor impurities in the lattice. One explanation is that Se vacancies are activated as a result of the doping process and lead to a compensation of the acceptor carriers. Other authors claim that it could be due to acceptors occupying interstitial sites along twin boundaries \(^{104}\) or the formation of acceptor-bound -exciton complexes with shallow
acceptors on a Se site. There is still a great deal of dispute on the exact mechanism limiting p-type conduction.

Nitrogen-doped ZnSe layers have been produced using several sources such as NH$_3$, Zn$_3$N$_2$, or N$^+$ ions. Characteristic emission of these films include emission of an I$_1$ line at 2.790 eV (444.39 nm) at 4.2 K. With increasing temperature, an upper energy line I$^h_1$ arises at 2.792 (eV) (444.08 nm). The energy spacing of the two lines is due to the strain split lh and hh valence band as explained earlier. A donor-acceptor-pair (DAP) series with a zero phonon line appears at 2.698 eV (459.55 nm) yielding an ionization energy of 101 MeV $^{105}$. Yoshikawa et. al. used NH$_3$ in low pressure OMVPE and showed that for large NH$_3$ flux, the I$_1$ and DAP lines were reduced indicating deep center formation involving N and chemical reactions with NH$_3$ preventing efficient diffusion of N into the layer $^{106}$.

Suemune et. al. found that N doping with perfectly matched ZnS$_{0.06}$Se$_{0.94}$ improves the crystal quality and doping properties as well as facilitates p-doping ($p=7\times10^{15}$ cm$^{-3}$, $\rho=21.9$ $\Omega$-cm) and weak Y and SA luminescence.

5.4.6 Donor-Acceptor-Pair Recombinations

In materials with both donors and acceptors present, new features in the PL spectrum refered to as donor-acceptor-pair recombinations (DAP) may be present. When impurity atoms are present in a lattice, it may form an electron or a hole which will occupy a specific energy state
within the forbidden band with an infinity of shallow excited states given by the Rydberg formula:

\[ E_n = - \left( m^* \frac{e^4}{2 \varepsilon_0 \varepsilon^2 n^2} \right) \quad n = 1, 2, \ldots \]

where \( m^* \) = effective mass
\( e \) = charge of an electron
\( \varepsilon \) = static dielectric constant

This also applies for p-type excited states for acceptor impurities.

Consider a n-type semiconductor with \( N_d \) donors and \( N_a \) acceptors per unit volume, at low temperatures such that \( E_{d,a} >> kT \).
Equilibrium between the conduction band and the valence band means that there will be \( N_a \) ionized donors and acceptors and \( N_d - N_a \) neutral donors. If excess electron hole pairs are injected into the material they may be trapped at ionized donors and acceptors. This leads to a number of neutral pairs of donors and acceptors as shown in figure 31.

![Figure 31. Donor-acceptor-pair recombinations.](image-url)
Donors and acceptors will recombine in isolated pairs to provide an elementary radiation recombination process at low temperatures. When the electron and hole are thermally stable on the donor and acceptor. The energy radiated depends on the d-a separation \( r \), but tends to \( E_g - (E_a + E_d) \) for large \( r \), as shown. These electron-hole pairs must recombine to restore equilibrium. Radiative recombination of these trapped pairs is the rate limiting process for dilutely doped semiconductor. Multiple phonon energy coupling of this transition is highly probable.

5.4.7 Doping Studies

Excitons readily bind to ionized donors or acceptors, neutral donors or acceptors, donor-acceptor pairs, or deep level isoelectronic impurities. The exciton binding energy to impurity atoms often depends on the ionization energy of the impurity. The bound exciton also exhibits LO phonon coupling in high quality films. The energy \( E_{BE} \) of the emission is

\[
E_{BE} = E_g - E_{X,n} - n\omega_{LO} \quad n=1,2,\ldots
\]

Table 1 lists the excitonic binding energies \( E_{BX} \) of several common impurities \(^{107}\).
Binding energies (meV) of bound excitons in ZnSe.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Ed</th>
<th>EBX</th>
<th>EBX</th>
<th>EBX</th>
<th>Acceptor</th>
<th>E_a</th>
<th>EBX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>neutral</td>
<td>weak</td>
<td>ionized</td>
<td>strong</td>
<td></td>
<td></td>
<td>neutral</td>
</tr>
<tr>
<td>Al</td>
<td>26.3</td>
<td>3.96</td>
<td>5.35</td>
<td>4.97</td>
<td>Li</td>
<td>114</td>
<td>9.5</td>
</tr>
<tr>
<td>Cl</td>
<td>26.9</td>
<td>4.05</td>
<td>5.76</td>
<td>5.36</td>
<td>Na</td>
<td>90-128</td>
<td>8.5</td>
</tr>
<tr>
<td>Ga</td>
<td>27.9</td>
<td>4.3</td>
<td>6.73</td>
<td>6.32</td>
<td>Cu_{deep}</td>
<td>200</td>
<td>18.5</td>
</tr>
<tr>
<td>In</td>
<td>28.9</td>
<td>4.5</td>
<td>7.62</td>
<td>7.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>29.3</td>
<td>4.6</td>
<td>8.02</td>
<td>7.62</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Binding energies of bound excitons in ZnSe.

The designation of excitonic emission is often labeled as $I_1$ for neutral acceptors and $I_2$ for neutral donors. Low temperatures are necessary for the observation of these transitions. At temperatures where $KT > E_{BX}$ or $E_{BE}$ the excitons will dissociate before they can radiatively recombine. The temperature for the onset of the observation of neutral donor bound excitons in zinc selenide is about 46 K. Table 2 and table 3 show the expected value of many of the donor and acceptor (respectively) dopant impurity bound excitons.
<table>
<thead>
<tr>
<th>line (eV)</th>
<th>line (nm)</th>
<th>line notation</th>
<th>$E_B(D^0,X)$ (meV)</th>
<th>donor</th>
<th>substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7974</td>
<td>443.22</td>
<td>$l'_2$</td>
<td></td>
<td>Ga</td>
<td>ZnSe</td>
</tr>
<tr>
<td>2.7969</td>
<td>443.30</td>
<td>$l_{20}$</td>
<td>3.8</td>
<td>Ga</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7971</td>
<td>443.26</td>
<td>$l^{Ga}_{20}$</td>
<td>4.3</td>
<td>Ga</td>
<td>ZnSe</td>
</tr>
<tr>
<td>2.7944</td>
<td>443.69</td>
<td>$l^{Ga}_{20}$</td>
<td></td>
<td>Ga</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7966</td>
<td>443.34</td>
<td>$l^{Ga}_{20}$</td>
<td></td>
<td>Ga</td>
<td>GaAs</td>
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<tr>
<td>2.7967</td>
<td>443.33</td>
<td>$l^{Ga}_{20}$</td>
<td>5.0</td>
<td>Ga</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7950</td>
<td>443.60</td>
<td>$l_{x}$</td>
<td>5.0</td>
<td>Ga</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7969</td>
<td>443.30</td>
<td>$l^{Ga}_{20}$</td>
<td>3.9</td>
<td>Ga</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7953</td>
<td>443.55</td>
<td>$l_{2}$</td>
<td>4.7</td>
<td>Ga</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7966</td>
<td>443.34</td>
<td>$l'_2$</td>
<td>3.4</td>
<td>strain-split</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7949</td>
<td>443.61</td>
<td>$l_{2}$</td>
<td>8.4</td>
<td>Ga</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7950</td>
<td>443.60</td>
<td>$l_{x}$</td>
<td>5.0</td>
<td>In</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7954</td>
<td>443.53</td>
<td>$l_{x}$</td>
<td>4.8</td>
<td>Cl</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7965</td>
<td>443.36</td>
<td>$l_{20}$</td>
<td>3.0</td>
<td>Cl</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7945</td>
<td>443.68</td>
<td>$l_{x}$</td>
<td>5.0</td>
<td>doublet</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7954</td>
<td>443.53</td>
<td>$l_{x}$</td>
<td>5.5</td>
<td>$V_{Se}$</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7954</td>
<td>443.53</td>
<td>$l_{x}$</td>
<td>5.5</td>
<td>$V_{Se}$</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7960</td>
<td>443.44</td>
<td>$l_{x}$</td>
<td>3.5</td>
<td></td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7968</td>
<td>443.31</td>
<td>$l'_2$</td>
<td>3.2</td>
<td></td>
<td>GaAs</td>
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<td>2.7948</td>
<td>443.63</td>
<td>$l'^2_2$</td>
<td>5.2</td>
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<tr>
<td>2.7960</td>
<td>443.44</td>
<td>$l_2$</td>
<td>3.0</td>
<td></td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7940</td>
<td>443.76</td>
<td>$l_{x}$</td>
<td>5.0</td>
<td>doublet</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7970</td>
<td>443.28</td>
<td>$l_{20}$</td>
<td>3.2</td>
<td></td>
<td>GaAs</td>
</tr>
<tr>
<td>2.8000</td>
<td>442.81</td>
<td>$l_{x}$</td>
<td>5.4</td>
<td></td>
<td>GaAs</td>
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</table>

Table 2. Donor-bound-exciton PL energies.
<table>
<thead>
<tr>
<th>line (eV)</th>
<th>line (nm)</th>
<th>line notation</th>
<th>$E_B(D_0,X)$ (meV)</th>
<th>donor</th>
<th>substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.7891</td>
<td>444.54</td>
<td>$I_{Li_1}$</td>
<td></td>
<td>Li</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7908</td>
<td>444.27</td>
<td>$I_{Li_1}$</td>
<td>doublet</td>
<td>ZnSe</td>
<td></td>
</tr>
<tr>
<td>2.7921</td>
<td>444.06</td>
<td>$I_{Li_1}$</td>
<td>10.6</td>
<td>Li</td>
<td>ZnSe</td>
</tr>
<tr>
<td>2.7918</td>
<td>444.11</td>
<td>$I_{Li_1}$</td>
<td>doublet</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7920</td>
<td>444.08</td>
<td>$I_{Li_1}$</td>
<td>Li</td>
<td>ZnSe</td>
<td></td>
</tr>
<tr>
<td>2.7890</td>
<td>444.55</td>
<td>$I_{S_1}$</td>
<td>10.0</td>
<td>Li</td>
<td>GaAs</td>
</tr>
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<td>2.7913</td>
<td>444.19</td>
<td>$I_{Li_1}$</td>
<td>12.0</td>
<td>Li</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7920</td>
<td>444.08</td>
<td>$I_{Li_1}$</td>
<td>triplet</td>
<td>Li</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7900</td>
<td>444.40</td>
<td>doublet</td>
<td>Na</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7930</td>
<td>443.92</td>
<td>$I_{Y_1}$ (Na)</td>
<td>Na</td>
<td>ZnSe</td>
<td></td>
</tr>
<tr>
<td>2.7830</td>
<td>445.51</td>
<td>$I_{deep_1}$</td>
<td>Cu</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7828</td>
<td>445.55</td>
<td>$I_{Nd_1}$</td>
<td>18.9</td>
<td>Cu</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7929</td>
<td>443.93</td>
<td>$I_{deep_1}$</td>
<td>Cu</td>
<td>ZnSe</td>
<td></td>
</tr>
<tr>
<td>2.7800</td>
<td>445.99</td>
<td>$I_{P_1}$</td>
<td>Cu or V$_{Zn}$</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7920</td>
<td>444.08</td>
<td>$I_{N_1}$</td>
<td>N</td>
<td>GaAs</td>
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</tr>
<tr>
<td>2.7900</td>
<td>444.40</td>
<td>$I_{Nd_1}$</td>
<td>11.0</td>
<td>N</td>
<td>GaAs</td>
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<tr>
<td>2.7917</td>
<td>444.12</td>
<td>$I_{Nd_1}$</td>
<td>N</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7917</td>
<td>444.40</td>
<td>$I_{I_1}$</td>
<td>11.0</td>
<td>N</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7910</td>
<td>444.08</td>
<td>$I_{Nd_1}$</td>
<td>9.0</td>
<td>N</td>
<td>GaAs</td>
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<tr>
<td>2.7916</td>
<td>444.24</td>
<td>$I_{I_1}$</td>
<td>11.0</td>
<td>N</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7920</td>
<td>444.14</td>
<td>$I_{Nd_1}$</td>
<td>9.9</td>
<td>N</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7920</td>
<td>444.08</td>
<td>$I_{Nd_1}$</td>
<td>10.7</td>
<td>N</td>
<td>ZnSe</td>
</tr>
<tr>
<td>2.7900</td>
<td>444.40</td>
<td>$I_{S_1}$</td>
<td>N</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7960</td>
<td>443.44</td>
<td>$I_{P_1}$</td>
<td>5.2</td>
<td>P</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7890</td>
<td>444.55</td>
<td>$I_{I_1}$</td>
<td>10.5</td>
<td>P</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7910</td>
<td>444.24</td>
<td>$I_{S_1}$</td>
<td>8.5</td>
<td>doublet</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7914</td>
<td>444.17</td>
<td>$I_{I_1}$</td>
<td>As</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7920</td>
<td>444.08</td>
<td>$I_{C}$</td>
<td>10.7</td>
<td>C</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7973</td>
<td>443.24</td>
<td>$I_{I_1}$</td>
<td>O</td>
<td>GaAs</td>
<td></td>
</tr>
<tr>
<td>2.7805</td>
<td>445.91</td>
<td>$I_{D_1}$</td>
<td>19.0</td>
<td>V$_{Zn}$</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7840</td>
<td>445.35</td>
<td>$I_{I_1}$</td>
<td>18.2</td>
<td>V$_{Zn}$</td>
<td>GaAs</td>
</tr>
<tr>
<td>2.7815</td>
<td>445.75</td>
<td>$I_{d}$</td>
<td>19.4</td>
<td>V$_{Zn-A}$</td>
<td>GaAs</td>
</tr>
</tbody>
</table>

Table 3. Acceptor-bound-exciton PL energies.
An enhancement of a specific donor-exciton line is expected to increase with increased concentration of the dopant. However, this assumes that the dopant acts as a simple substitutional impurity atom. Often a more complex donor center or even an acceptor center may be formed which attributes to compensating deep centers such as \( \text{V}_{\text{Zn}} - \text{GaSe} \) \(^{109}\).

Line shapes and line widths of spectral features often give information about film quality. Polycrystalline films exhibit broader bound exciton features than single crystal material. Typical line widths can be as narrow as 1 meV for single crystal zinc selenide but up to several meV due to strain in the films. Polycrystalline material often has spectral widths of 10 meV for these transitions. Temperature effects also greatly increase the spectral line widths of these feature due to lattice vibrations.

Some of the wavelength values for various transitions have been collected from different publications and are shown in table 4.
<table>
<thead>
<tr>
<th>Transition</th>
<th>$\lambda$(nm)</th>
<th>$\lambda$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_x^1$ free exciton (FE)</td>
<td>442.491</td>
<td>2.802</td>
</tr>
<tr>
<td></td>
<td>heavy-hole (hh)</td>
<td></td>
</tr>
<tr>
<td>$E_x^2$ free exciton (FE)</td>
<td>442.807</td>
<td>2.800</td>
</tr>
<tr>
<td></td>
<td>light-hole (lh)</td>
<td></td>
</tr>
<tr>
<td>$I_2^1$ donor bound exciton (DBE)</td>
<td>443.3</td>
<td>2.797</td>
</tr>
<tr>
<td>undoped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I_2^2$ donor bound exciton (DBE)</td>
<td>443.59</td>
<td>2.795</td>
</tr>
<tr>
<td>undoped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I_1^1$ acceptor bound exciton (ABE)</td>
<td>444.39</td>
<td>2.790</td>
</tr>
<tr>
<td>(nitrogen)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$I_1^2$ acceptor bound exciton (ABE)</td>
<td>444.076</td>
<td>2.792</td>
</tr>
<tr>
<td>(nitrogen)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_0$ donor-acceptor-pair (DAP)</td>
<td>459.2</td>
<td>2.698</td>
</tr>
<tr>
<td>(nitrogen)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_1$ donor-acceptor-pair (DAP)</td>
<td>463.0</td>
<td>2.677</td>
</tr>
<tr>
<td>phonon coupled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Y_0$ structural defects</td>
<td>476.8</td>
<td>2.60</td>
</tr>
<tr>
<td>$S_0$ self activated (SA)</td>
<td>619.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 4. Wavelength values of commonly observed photoluminescence peaks in zinc selenide.
Chapter 6
Results

6.1 Experimental overview

Experiments concerning the growth of nitrogen doped ZnSe epilayers on GaAs have been performed in order to evaluate the growth conditions within the reactor and to optimize the parameters for growing high quality films. The quality of the films can be evaluated by observing their optical properties (photoluminescence), electrical properties, and morphology. In order to make an accurate appraisal of the optimization of particular growth parameters, it was necessary to hold the other parameters as constant as possible from growth to growth. Some of the growth parameters which were always kept constant in these experiments include:

1) Mass flow rates of hydrogen and metal organic sources.
2) Total chamber pressure (100 Torr).
3) Growth procedure - pump out, heating and cooling rates, etc...
4) Sample mounting, geometry, preparation, etc..
5) Laser parameters - ArF laser (193 nm), optical configuration, power (100 mJ/pulse), repetition rate (10 Hz).

6.1.1 Undoped ZnSe

The first set of experiments was to establish growth rate curves for undoped ZnSe on the reactor with and without laser assistance. Growth
rate curves are necessary in device applications when layers of known thickness are desired. Growth-rate curves were established by growing films at different temperatures for a constant time of 20 minutes, yielding a series of films ranging in thickness from 0.1 \( \mu \text{m} \) to 1.3 \( \mu \text{m} \). The thickness was measured by interferometry using an optical microscope (described elsewhere). The data is plotted as the log of the growth rate versus inverse temperature where the slope of the line is proportional to the activation energy of the growth process, assuming that the growth rate follows Arhenius behavior of the form

\[
\text{Rate} = A \exp\left(-\frac{E_a}{kT}\right).
\]

The initial growth rate curves were then used to determine the time of growth for constant thickness (0.8\( \mu \text{m} \)) films grown at different substrate temperatures. A consistency in the film thickness eliminates PL features which may be due to unequal strain from film to film such as the presence or absence of misfit dislocations.

The effect of growth temperature on the film quality was primarily evaluated by the photoluminescence (PL) spectra. PL spectra are a very good indication of crystalline quality and can be correlated to good electrical properties.

6.1.2 Nitrogen-Doped ZnSe Films

ZnSe can be doped with nitrogen to produce p-type conduction. Nitrogen has been shown to be a potentially useful shallow acceptor in ZnSe and has been incorporated into ZnSe films by low pressure
MOVPE. Nitrogen can be incorporated into the films from anhydrous ammonia (NH₃). In the experiments reported here, electronic grade ammonia (99.999%) was used to dope films during growth. Ammonia is a thermally very stable source and is difficult to incorporate into the films by conventional MOCVD techniques. However, our experiments attempt to increase the solubility of nitrogen from ammonia in ZnSe by two methods:

1) Using the ArF excimer laser to aid in the dissociation of the NH₃ molecule.

2) Using a non-equilibrium condition during growth by direct surface irradiation.

NH₃ is a good candidate for acceptor incorporation into the films by laser-assisted MOCVD because it has its peak cross section of absorption in the ultraviolet at around 194 nm. Therefore the ArF (193 nm) is a very suitable choice in the photodissociation of the ammonia. The photodissociation of NH₃ is as follows:

\[ \text{NH}_3 + \text{hv} \rightarrow \text{NH}_2 + \text{H} \]

This reaction would require a great deal of thermal energy if the ArF excimer laser was not used. The reaction does not produce free nitrogen atoms but the reduced species may further react on the surface to incorporate nitrogen into the ZnSe films. Previous work used NH₃
mass flow rates almost as high as the selenium source. Laser-assisted MOCVD allows the mass flow rate to be around 1/10 of the selenium source mass flow rate.

When the surface of the film is irradiated during growth with a broad-band light source (100 W xenon lamp), photons with energy greater than the band gap of ZnSe create electron-hole pairs in the film. This non-equilibrium condition of free carriers has been shown to greatly increase the growth rate. The mechanism may involve the free carriers reacting on the surface with charged radicals to help remove them. Neumark has done a thermodynamic analysis and shown that p-type conduction in several II-IV semiconductors is not even possible without a non-equilibrium condition (as opposed to self compensation theory).

The effect of doping ZnSe with nitrogen was investigated by analyzing the photoluminescence spectra of the films as a function of NH₃ mass flow rate. Experiments were performed at a constant substrate temperature of 475 °C and with the excimer laser set at 100 mJ/pulse with a repetition rate of 10 Hertz. The NH₃ flow rate was varied from 0.5 to 10 sccm until an optimum flow rate regime could be determined.

Direct irradiation experiments were performed to examine the wavelength and intensity dependence of the incident light. Samples were irradiated during growth with broad-band radiation from a 100 watt xenon lamp. Wavelength dependence was examined using a low pass cutoff filter. The growth rate was examined for films grown under identical conditions except for the placement of a Corning 3-70 yellow
glass filter which allowed only passed below band-gap photons to reach the film.

The intensity dependence of the direct irradiation has also been investigated. The direct irradiation intensity was changed from 0 to 175 mW/cm² by adjusting the lamp current and using neutral density filters. The power was calibrated in-situ previous to the experiments using a broad-band photo detector with a 1 cm² mask on the detector surface which was placed in the position of the sample during growth. Growth rates were measured using an interference microscope objective. Photoluminescence spectroscopy was used to determine film quality and nitrogen incorporation at different growth rates.

6.2 Experimental Results

6.2.1 Undoped ZnSe Films

There are many parameters which can be varied during the growth process. To reduce the total number of experiments needed for optimization, several parameters were held fixed throughout the experiments. Substrate temperature was the primary variable which was optimized for our reactor configuration. Previous research (Shinn et. al.44) determined values for many of the other parameters. Conditions which remained constant in the growth process throughout the entire set of experiments are listed in table 6.
Mass flow rate DMZ = 2.16 sccm  
Mass flow rate DES = 25.23 sccm  
Mass flow rate total = 2017.39 sccm  
Se/Zn ratio= 11.67 : 1  
H₂ dilution = 73.6 : 1  
Velocity (inner tube) = 23.9 cm/s  
Total chamber pressure = 100 Torr  
Excimer laser power = 100 mJ  

Table 5. MOCVD Reactor Conditions

A ratio (VI:II) of about 10:1 is commonly used in many epitaxial growth processes because the growth is limited by the transport of the group II species. A hydrogen flow rate ratio of 10:1 was used in the metal organic constant temperature bubblers yielding the values listed in table 6. Hydrogen carrier gas is the main component of the total flow. The velocity of the flow in the inner tube was chosen to be in the laminar flow regime estimated by classical hydrodynamics. Exact analysis of the flow behavior is difficult due to the particular geometry and the complexity of the reactor. Convection should not be a problem with the inverted substrate design and the flow can be modeled as laminar flow between two parallel plates. The velocity of the H₂ purge gas in the outer tube was chosen to closely match the velocity in the inner tube. The mass flow rates of the window purge gas were held constant once sufficient window cleanliness could be maintained.

6.2.2 Substrate Temperature

To analyze the effect of substrate temperature on film quality, it was necessary to grow a series of films at constant thickness at different
temperatures and compare the PL spectra. To determine the time necessary to grow films of a certain thickness at a given temperature, a growth rate curve had to be established. This was done by growing films at different temperatures for a fixed time (30 minutes), measuring the thickness, and making a plot growth rate vs substrate temperature. From this, the proper time to grow films of a constant thickness could be determined from the growth rate at that temperature. Figure 31 shows the initial growth rate curve for samples grown for 30 minutes at different substrate temperatures.

Figure 32. Initial growth rate curve for samples growth for 30 minutes.

Samples were then grown to a constant temperature of ~0.8 μm according to the growth rate at that particular temperature. Figure 33
shows a plot of the ln (growth rate) as a function of 1/T(K) for the films which were grown to a thickness of 0.8 μm.

Figure 33. Growth rate curve for laser-assisted MOCVD ZnSe films of constant thickness (~0.8 μm).

A series of photoluminescence experiments was performed on these films to optimize the growth parameters of undoped zinc selenide films for the present reactor design. Indications of film quality were primarily determined by low temperature photoluminescence spectroscopy. The primary indication of the lack of quality of the film is the presence of a broad-band peak in the 500 nm region of the spectrum known as the "self-activated" peak which is associated with structural
irregularities in the film such as dislocations, vacancies, point defects, and crystallinity as discussed in chapter 5. The presence of this peak indicates poor film quality. Photoluminescence spectroscopy was performed on the films at 8 K as described in chapter 5. A three-dimensional plot of the corresponding PL spectra as a function of substrate temperature are shown in figure 34.

Figure 34. Photoluminescence spectra of undoped ZnSe as a function of substrate temperature.

The dominant emissions in the PL spectra are the "self-activated" peak around 540 nm and the donor-bound -exciton emissions at 443.3 nm designated as Ix (or I2) which are considered to originate from excitons bound to neutral donors from unintentional impurities such as
chlorine. The free exciton emission $E_X$ is not easily resolved except in the film grown at 475 °C. The "self-activated" emission associated with deep level emission shows a strong substrate temperature dependence and is the dominant feature in films grown at temperatures below 450 °C. At lower growth temperatures, the self activated emission may be caused by the formation of defect complexes because of a lower surface mobility of the atoms as they attempt to arrange crystallographically. Many of the films grown at temperatures $\geq 500$ °C typically lacked the presence of a free exciton peak and showed several lines which were initially difficult to identify. The presence of excitonic emission at ~446 nm which is present in the films grown at higher temperatures was found to be associated with oxygen incorporation and also usually has a $I_{\text{Deep}}$ line at ~451 nm associated with it. The oxygen incorporation only appeared in films grown at higher temperatures and therefore may be thermally activated at temperatures above 500 °C. Higher growth temperatures increase the concentration of intrinsic defects such as vacancies and also increase the solubility of impurity atoms. Improvements in the reactor vacuum system were made to reduce the oxygen incorporation. The addition of a diffusion pump to allow the system to be pumped to $10^{-6}$ torr prior to growth, greatly reduced the presence of oxygen related defects.

The optimum growth temperature was determined by evaluating the PL spectra for (1) the presence of the free exciton line, (2) low self-activated line, (3) and few defect levels. The PL spectra for films grown at temperatures $\leq 450$ °C a were characterized by a large self-activated peak. The PI spectra for films grown temperatures $\geq 500$ °C lacked free
excitonic emission and contained numerous defect levels near the band edge. The optimum spectra for undoped zinc selenide was determined to be 475 °C because of a well resolved free exciton peak, low self activated emission, and few defect levels present. The presence of a free exciton peak indicates a lack of crystalline defects such as vacancies and dislocations which can cause the free exciton to become bound. Other authors of MOCVD growth have found optimum growth temperatures to be around 400 °C. This difference may be due to the technique of temperature measurement. The actual substrate surface temperature can be significantly lower than the temperature measured within the stainless steel substrate holder. A plot of the PL spectrum of undoped ZnSe grown at 475 °C is shown in figure 35.

Figure 35. Photoluminescence of undoped ZnSe grown at 475 °C.
The PL spectrum shows very strong excitonic emission which has been resolved into the free exciton $E_x$ at 442.44 nm (2.802 eV) and the donor bound exciton $I_2$ at 443.28 nm (2.797 eV). The presence of the strong free exciton peak is a very good indication of a high quality film. The self-activated is not even observable on this scale. A very small "Y" line can be observed around 476 nm indicating the presence of some dislocations as can be expected for a 0.8 µm film.

A photoluminescence spectrum of an unintentionally doped sample grown at 525 °C is shown in figure 36.

![Photoluminescence spectrum of undoped ZnSe grown at 525 °C.](image)

Figure 36. Photoluminescence spectrum of undoped ZnSe grown at 525 °C.

The dominant features are the presence of several excitonic peaks near the band edge. The donor-bound -exciton emission $I_2$ is located at 443.4 nm. The largest peak appears to be a peak at 445.7 nm (labeled $I_0$). This
peak has been attributed to oxygen occupying interstitial sites in the ZnSe lattice. A deep acceptor peak I_{Deep} is also found at 450.9 nm.

It is important to note that the temperature measurement of these experiments is unique to the geometry of our reactor. The measurement was made by a type J thermocouple positioned in the center of the stainless steel substrate holder. The exact temperature at the substrate surface is not measured and therefore growth temperatures at the sample surface are probably lower than indicated. These growth temperatures are somewhat higher than others listed in the literature. 475 °C was taken as the optimum growth temperature and was then used in the study of nitrogen-doped zinc selenide from NH₃.

6.2.3 Nitrogen-Doped Films

In order to examine the effect of nitrogen incorporation into the ZnSe films, a series of experiments was performed introducing electronic grade ammonia (NH₃) into the growth reactor. The mass flow rate could be carefully controlled using a Unit Instruments mass flow controller calibrated for a full flow of NH₃ of 20 sccm. Purging of the flow meter with UHP nitrogen is necessary before and after each growth to prevent corrosion.

A series of experiments was performed varying the mass flow rate of the NH₃ from 0 to 10 sccm and maintaining the optimized reactor conditions obtained from the undoped experiments. The PL spectrum of nitrogen doped films appears quite different from the undoped films.
Figure 37 shows a PL spectrum of a nitrogen-doped ZnSe film grown at 475 °C with a NH₃ mass flow rate of 2 sccm.

![Spectrum Image]

Figure 37. Photoluminescence (8 K) spectrum of a nitrogen-doped ZnSe film grown at 475 °C with a NH₃ mass flow rate of 2 sccm. The insert shows the spectrum of the excitonic region.

In the PL spectrum, a donor-acceptor (D-A) pair emission band Q₀ is dominant with a zero phonon peak centered at 458.9 nm and several phonon coupled replicas at around 463.3, 467, and 472 nm. In the excitonic region, I₁ originating from an exciton bound to neutral shallow nitrogen acceptors is clearly observed. These lines are indicative of shallow acceptor centers in the films. The presence of a very large free exciton peak Eₓ is also a very good indication of very high quality
material. The donor-bound exciton peak $I_2$ is also still present indicating that a shallow donor level is also present. The presence of the nitrogen acceptor-bound-exciton and the nitrogen donor-acceptor-pair emission confirm successful doping of nitrogen into ZnSe epitaxial films by laser-assisted MOCVD.

To examine the influence of the importance of the ArF excimer laser on film growth of nitrogen doped films, a thermal sample was grown under the exact same conditions as sample 11-23-91L1 as in figure 36 without the assistance of the excimer laser. The PL spectrum of this film is shown in figure 38.

![Spectrum Diagram]

**Figure 38.** Photoluminescence spectrum of a nitrogen-doped, thermal ZnSe film grown at 475 °C with a NH$_3$ mass flow rate of 2 sccm. The insert shows the spectrum of the excitonic region.
This spectrum is similar to the laser-assisted film in some of the features. Both show donor-acceptor-pair recombination emission and the phonon coupled replicas at 459 nm and 463 nm indicating nitrogen incorporation. Both films show free exciton emission at 442.3 nm and donor-bound-exciton emission at 443.3 nm. The thermal film, however, lacks the presence of acceptor-bound-exciton emission at 444 nm. It does show an oxygen related emission I_O at 445.5 nm and a deep acceptor line I_Deep at 450.6 nm.

In order to investigate the effect of the dependence of the NH_3 mass flow rate on laser-assisted MOCVD grown films, a series of films were grown under identical reactor conditions with 0 to 10 sccm of NH_3 introduced. Figure 39 shows a three dimensional plot the 8 K PL spectra of the normalized intensities as a function of NH_3 mass flow rate.

![Figure 39. Dependence of the photoluminescence spectra of nitrogen-doped ZnSe films on the flow rate of NH_3 gas.](image-url)
When the flow rate of the NH$_3$ is low ($\leq$ 3 sccm), the I$_1$ and D-A pair emission can be observed and are clearly resolved in the film grown with a mass flowrate of 2 sccm. At higher flow rates the near band edge emission broadens and the peaks become unresolvable, centered at the donor-bound-exciton emission, and emission from shallow acceptors is not observed. The broadening in the excitonic emission region with increased flow rates may be caused by the presence of defect centers and/or strains which are caused by the incorporation of larger amounts of nitrogen into the films. Yoshikawa reported similar excitonic emission broadening also with an increase in mid-band defects $^{116}$. The ratio of the intensity of the D-A pair emission to the excitonic region increases as a function of the mass flow rate of NH$_3$ as shown in figure 40.

![Graph](image)

Figure 40. Increase in ratio of D-A pair emission intensity to excitonic emission as a function of mass flow rate of NH$_3$. 
The increase in the ratio of $Q_0/BE$ emission indicates that the amount of nitrogen incorporated into the films increases with increasing mass flow rates. However, at the higher flow rates the broadening of the excitonic emission implies that the film quality is reduced because of strain or defect complexes which may be forming.

6.3 Non-equilibrium Direct Irradiation Effects

The effect of direct irradiation from a xenon lamp normal to the growth surface has also been investigated. A 100 W xenon lamp was placed beneath the MOCVD reactor such that the light could pass through a BK-7 glass viewport onto the mounted sample. The configuration is shown in figure 41.

Figure 41. Direct irradiation growth configuration
The xenon lamp has a relatively flat, broad-band spectrum which extends from about 300 nm to 1 μm. The glass viewport cuts off wavelengths less than about 350 nm. The interaction of the radiation with source gases is not expected since the xenon lamp radiation is not effectively absorbed by the source precursors. The intensity can be adjusted to a maximum of about 500 mW/cm² by focusing the optics and adjusting the current of the lamp. Neutral density filters may be used to reduce the intensity.

6.3.1 Wavelength dependence

The wavelength dependence of direct irradiation has been shown by Fujita⁸⁰ to have an important effect on the growth rate. The mechanism of direct irradiation effects remains an important topic for investigation. Growth rate enhancement has been shown to occur when the growth surface is irradiated with above band gap photons during growth even at temperatures when there is insufficient thermal energy to promote normal growth. To confirm this, two samples were grown under identical conditions, with the exception of a low-pass cutoff filter (Corning 3-70 yellow glass filter) which cuts off above 500 nm, to prevent above band-gap photons from irradiating one sample. The results are shown below:
<table>
<thead>
<tr>
<th>Sample</th>
<th>7-30-9211</th>
<th>7-29-9211</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity (mW/cm²)</td>
<td>175</td>
<td>175</td>
</tr>
<tr>
<td>Filter</td>
<td>3-70</td>
<td>none</td>
</tr>
<tr>
<td>$T_{sub}$</td>
<td>400 °C</td>
<td>400 °C</td>
</tr>
<tr>
<td>M(NH₃)</td>
<td>2 sccm</td>
<td>2 sccm</td>
</tr>
<tr>
<td>Time</td>
<td>15 min.</td>
<td>10 min.</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.07 µm</td>
<td>0.464 µm</td>
</tr>
<tr>
<td>Growth Rate</td>
<td>~0</td>
<td>2.36 µm/hr.</td>
</tr>
</tbody>
</table>

Table 6. Wavelength Dependence of Direct Irradiation Growth

The sample grown with the filter in place had virtually no growth except for a 400 Å ZnSe buffer layer which was initially deposited at 475 °C for 2.5 minutes. The sample without the filter exhibited significant growth rate at this temperature which is in the reaction-limited range. Without the buffer layer, no photo-enhanced growth was observed. The growth enhancement mechanism therefore requires the formation of a small ZnSe layer before it can be initiated. The above band-gap irradiation is therefore responsible for the growth rate enhancement. The creation of electron-hole pairs in the ZnSe epilayer must also be involved in the growth process process.

6.3.2 Intensity dependence

Experiments were performed to investigate the direct irradiation intensity dependence by growing films at different irradiation intensities under the same reactor conditions (a substrate temperature of 400 °C and with an ammonia mass flow rate of 2 sccm). The growth rate would be very low at this temperature with thermal MOCVD. The intensity was
varied from 0 to 175 mW/cm². A 400 Å ZnSe buffer layer was initially
grown at 475 °C for 2.5 minutes. This is necessary to initiate the growth
enhancement mechanism. The most pronounced effect of the direct
irradiation was a large enhancement of the growth rate as shown in
figure 42. Growth rates were measured with an optical microscope using
an interferometer objective.

![Graph](image)

Figure 42. Growth rate enhancement of nitrogen-doped ZnSe films
grown at 400 °C by direct irradiation.

The growth rate shows an almost linear increase with direct
irradiation intensity. The increased growth rate at 175 mw/cm²
corresponds to thermal MOCVD growth rates at about 500°C. This tends
to support the role of photo-generated carriers.
Photoluminescence spectra were taken of films as a function of direct irradiation intensity and are shown in a three dimensional plot as a function of increasing direct irradiation intensity in figure 43.

![Figure 43](image)

Figure 43. Photoluminescence spectra as a function of increasing direct irradiation intensity.

The spectra of the samples grown at different irradiation intensities (i.e. different growth rates) appear very similar. They are dominated by an intense donor-acceptor pair recombination peak, associated with nitrogen acceptors, at 458 nm (Q₀) and its phonon-coupled replicas at
463 nm. There is virtually no mid-band defects present, "Y-line", or indication of self-activated emission. The are excitonic peaks at the near band edge around 443.6 nm which have been resolved in some samples as shown in figure 44.

![Graph of Intensity vs Wavelength](image)

Figure 44. Near band edge photoluminescence of nitrogen-doped ZnSe film grown at 400 °C under direct irradiation intensity of 20 mW/cm².

The free-exciton peak ($E_X$) is observed at 442.7 nm. The donor-bound exciton ($I_2$) is observed at 443.6 nm. The acceptor-bound exciton ($I_1$) is observed at 444.4 nm. This sample indicates that very high quality nitrogen doped films can be grown by direct irradiation at temperatures
lower than by thermal MOCVD and there is high potential for this technique in the development of opto-electronic devices.

6.3.3 Discussion of Growth Rate Mechanisms

To better understand the chemical growth processes in photo assisted MOCVD, experiments were performed examining the interaction of the laser assisted technique while directly irradiating the growth surface with the broad band xenon lamp. The ArF excimer laser photodisassociates the precursor gases changing the chemistry of the mechanism in which either zinc or selenium atoms are transported to the surface and incorporated into the lattice. Experiments have been performed at Rice University involving time resolved absorption experiments of dimethylzinc as it is photodissociated by 193 nm radiation from the ArF excimer laser. The results confirm that nearly 100% of the dimethylzinc molecules are photodissociated into atomic zinc and methyl radical and have a lifetime of several milliseconds. The methyl radicals strongly tend to combine and form ethane (C₂H₆) according to reaction rate constants published by the National Bureau of Standards. Likewise, selenium atoms can be expected to form from diethylselenide. The atomic species travel very rapidly to the surface where they can be incorporated into the lattice.

Growth mechanisms of direct surface irradiation in MOCVD have been determined to involve the creation of free electrons and holes from the absorption of photons greater than the band gap (~ 450 nm for ZnSe).
of the material being deposited and less than the absorption region of the precursors (< 300 nm). The growth rate has been determined to be proportional to the intensity. The growth rate enhancement is observed in the reaction-limited growth regime. One likely mechanism is the removal of alkyl groups from the surface when there is insufficient thermal energy by oxidation reactions from holes generated by the irradiation. With the aid of photoinduced positive holes, the decomposition of DES of a zinc stabilized surface is enhanced. The same is true for the decomposition of a DMZ on a selenium terminated surface. Figure 45 shows a plausible reaction models for the reaction of DMZ and DES at the surface.

![Chemical structures](image)

Figure 45. Possible reaction mechanism for the direct elimination of alkyls from dimethylzinc and diethylselenide precursors.

In this mechanism, the activation energy for the reaction of alkyl removal from DMZ and DES is reduced by the presence of excess holes, thus liberating an alkane such as C₃H₈. It may be possible that the holes directly reduce the bond strength of metal organic molecules allowing the chemisorption of the zinc or selenium atom and liberating radicals which
can combine to form \( \text{C}_2\text{H}_5 \) and \( \text{C}_4\text{H}_{10} \). There may be other similar type reactions which may also be occurring.

An experiment was performed to investigate the effect of direct illumination with a broad band xenon lamp as well as using the ArF excimer laser to photodissociate the precursors. The purpose was to examine the growth rates to determine if direct illumination reaction mechanisms occur if the precursors reach the surface in atomic state.

The experiment was performed by masking the xenon lamp so that only half of the sample was illuminated while the ArF excimer laser passed parallel to the surface. Thus, the exact same growth conditions could be present for each region of (1) ArF laser plus direct irradiation, and (2) ArF laser only. The sample had a growth temperature of 400 °C which is low enough to prevent growth by thermal mechanism. The laser had an energy of \(~80\) mJ/pulse and a repetition rate of 10 hertz.

The results showed that the film exhibited a growth rate in the directly irradiated region (1) greater than that of the region (2) with only the ArF laser. The region with the xenon lamp irradiation and the excimer laser had a thickness of 0.546 \( \mu \text{m} \), corresponding to a growth rate of 2.18 \( \mu \text{m/hr} \). The region of just the ArF laser had a thickness of 0.389 \( \mu \text{m} \), corresponding to a growth rate of 1.55 \( \mu \text{m/hr} \). The direct photo irradiated mechanism as well as the ArF laser assistance obviously both contribute to the growth rate enhancement. Because the ArF excimer laser is pulsed, there exists time between pulses in which both the laser assisted mechanism and the alkyl elimination mechanism may both be occurring. The time between pulses is 100 milliseconds. The ArF laser
beam profile is approximately 1 cm wide in the growth region. The velocity of the gases in the reactor is 24 cm/s. Thus, the gases travel a distance of 2.4 cm in the time between pulses. This is enough time to allow new precursor molecules to come in contact with the surface and initiate growth by means of one of the direct photo irradiated mechanisms.

A second experiment was performed in which the ArF laser repetition rate was increased and the velocity of the flow was reduced to lower the growth occurring by direct reaction of the metal alkyls with the surface in the time between laser pulses. The ArF excimer laser was maintained at the maximum repetition rate of 20 hertz. The velocity of the gases was reduced to about one forth or ~6 cm/s. These changes limited to gases to travel a distance of about 0.3 cm through the ArF laser beam path. The sample showed a consistent thickness profile indicating that the photo enhanced growth mechanism did not occur in the laser irradiated area.

These results are consistent with the postulated growth rate mechanisms of both laser assisted MOCVD and direct surface irradiation photo MOCVD. The ArF laser assisted growth rate mechanism involves the incorporation of zinc and selenium atoms in atomic state. The direct surface irradiation involves the interaction of alkyls with photogenerated free electrons and holes.
Chapter 7

Conclusions and Recommendations

7.1 Conclusions

The potential for the economical development of high quality wide band gap semiconductors is enormous. Blue ZnSe-based LED's and laser diodes have now been fabricated which operate efficiently at liquid nitrogen temperatures (77 K)\(^{117}\). Room temperature operation of these devices is very close to becoming possible. Economical processes such as vapor phase epitaxy must now be developed to realize the application of these devices. This thesis has investigated nitrogen doping of ZnSe epitaxial films on GaAs by laser-assisted MOCVD for the development of p-type material which may be used in device applications.

A growth reactor has been designed and constructed which accommodates laser irradiation parallel to the sample and also allows direct surface irradiation from a broad-band light source. The sample is mounted inverted on the top wall of a horizontal, rectangular flow tube which minimizes convective flow problems and eliminates particulate incorporation from gas phase nucleation processes. The design also allows convenient sample loading and removal. Other improvements in the previously existing MOCVD system include the installation of a diffusion pump and the ability to bake out which has reduced background impurity levels such as oxygen.
Undoped ZnSe has been grown at different substrate temperatures. The films grown at 475 °C exhibited very good photoluminescence spectra with strong free and donor-bound-exciton emission, and very low "self-activated emission". Films grown at lower temperatures exhibited much higher self activated emission indicating poor film quality. Films grown at higher temperatures lacked free exciton emission and exhibited deep acceptor emission from background impurities such as oxygen. All of the films were grown to a constant thickness of ~0.8 μm. ArF excimer laser radiation has been shown to increase the growth rate at lower substrate temperatures and improve PL quality.

Nitrogen doping of ZnSe was investigated by introducing NH₃ into the growth region at flow rates from 0 to 50 sccm. The best films had NH₃ mass flow rates comparable to the DMZ flow rate (~ 2 sccm). Conventional MOCVD reactors in the literature required flow rate 10 times higher than this (~ 25 sccm). The incorporation of nitrogen as a shallow acceptor is clearly obvious in the PL spectra by the presence of a strong acceptor-bound-exciton peak and associated donor-acceptor-pair recombination emission. Very high quality films have also been demonstrated by the presence of a strong free-exciton peak. Nitrogen doped films grown by laser-assisted MOCVD had very little mid-band emission. The ArF excimer laser has been shown to enhance nitrogen incorporation. We have demonstrated PL spectra of nitrogen doped films comparable to any published in the literature.

The dependence on the NH₃ flow rate was investigated. It was found that the nitrogen incorporation increases as a function of NH₃ flow
rate based on the ratio of DAP emission (Qo) to the donor-bound-exciton emission. Although, as the flow rate was increase above 5 sccm, peak broadening occurred indicating the presence of the formation of defect complexes.

The effect of direct broad-band irradiation incident on the sample surface has been investigated. Direct irradiation creates a non-equilibrium condition at the surface of the sample by the creation of electron-hole pairs which affects the chemistry at the growth surface. Growth rate enhancement has been demonstrated as a function of irradiation intensity with growth rates up to 2 μm/hour observed at temperatures where thermal growth rates are extremely low. Films grown at intensities >100 mW/cm² exhibited a cloudy or rough morphology indicating polycrystalline growth. This may be explained by the rapid growth rate. Films irradiated with light below the band gap of ZnSe exhibited essentially no growth. Reaction mechanisms have been proposed involving the interaction of positively charged holes to assist in the removal of alkyls from the surface or the reactants.

Growth rate mechanisms have been postulated to explain laser assisted MOCVD and direct irradiation photo assisted MOCVD. Experiments have been performed to verify proposed growth mechanisms involving ArF excimer laser assisted growth simultaneously with direct surface irradiation from a xenon lamp. The ArF laser photodissociates the precursors resulting in zinc and selenium atoms to reach the surface in atomic state. Therefore, direct irradiation should not enhance the growth rate by the proposed alkyl elimination growth mechanisms. By increasing the laser repetition rate and decreasing the
flow velocity, we have confirmed that direct photo irradiation does not enhance the growth rate during laser assisted MOCVD.

7.2 Recommendations

Optimization of any semiconductor growth process is never complete. There are many parameters and procedures of the growth which could be investigated or improved. Some of the growth parameters which were generally held constant but could be further investigated include total pressure, total flowrate, ratio of zinc to selenium, hydrogen dilution, laser power and laser repetition rate. Some of the growth procedures which could be further investigated include substrate temperature measurement, substrate processing and mounting, laser alignment, and thermal processing during growth.

This research has optimized certain growth parameters based on the photoluminescence spectra of each sample. Further characterization techniques would be very beneficial to developing devices quality material. Electrical properties characterization must be reliably developed which can determine net carrier concentration and/or carrier mobility. Because of the difficulty in obtaining ohmic contacts to p-type ZnSe, capacitance-voltage techniques such as planar C-V profiling appear promising.

The quality of MOCVD grown films is often limited by the purity of source materials. Chemical analysis by Secondary Ion Mass Spectroscopy (SIMS) may be useful in determining impurity concentrations and dopant incorporation. New sources may be
necessary such as hydrogen selenide as a selenium source. New nitrogen sources may also need to be examined. To develop p-n junction devices, n-type dopant sources will need to be added to the system. Better lattice matching to the GaAs substrate may also show to be beneficial be the addition of sulfur to form lattice matched ZnS_{1-x}Se_x.

Improvements have been made in reducing background impurities by installing a diffusion pump. Further improvements can still be made by improving the vacuum integrity of the system. Quadrupole mass spectrometer measurements have showed that the background levels rise when the pumping system is closed off. Helium leak checking, however could not reveal a leak. Outgassing from the walls which may account for this could be reduced by overnight baking of the system. The design and installation of a load-lock may also be beneficial.

Improvements to the understanding of the laser-assisted MOCVD growth mechanisms of ZnSe are constantly advancing. New short pulse laser techniques may answer some of the questions about photo-assisted reactions of source gases which yield insight to improvements in the growth process. Once net p-type carrier concentrations above at least 10^{16} cm^{-3} can be sucessfully produced, p-n junction diodes should be grown on conducting and characterized to determine their electrical and luminescence behavior.
References


Appendix A

Physical Properties of Zinc Selenide

lattice parameter (ZnSe) 5.6693 Å
lattice parameter (GaAs) 5.6533 Å
Molecular weight (ZnSe) 144.3 g/mole
Molecular weight (GaAs) 144.7 g/mole
Density (ZnSe) 5.42 g/cm³
Density (GaAs) 5.317 g/cm³
$\alpha_{\text{ZnSe}}$ thermal expansion coef. 6.84 x 10⁻⁶ K⁻¹
$\alpha_{\text{GaAs}}$ thermal expansion coef. 5.80 x 10⁻⁶ K⁻¹
Thermal conductivity (ZnSe) 0.19 W/cm K
Thermal conductivity (GaAs) 0.70 W/cm K
Cₚ Heat Capacity 12.4 cal/mole K
elastic constant C₁₁ 8.59 x 10¹⁰ N/m²
elastic constant C₁₂ 5.06 x 10¹⁰ N/m²
elastic constant C₄₄ 3.92 x 10¹⁰ N/m²
σ₀ Poisson's ratio C₁₁/(C₁₁+C₁₂) 0.38
Kᵣ isothermal compressibility 1.46 x 10⁻¹¹ m² N⁻¹
Kₛ adiabatic compressibility 1.56 x 10⁻¹¹ m² N⁻¹
Band gap 4K 2.83 ev (438.11 nm)
Band gap 300 K 2.67 ev (464.37 nm)
m*ₙ 0.17
m*ₚ 0.7
low frequency dielectric constant 8.1 - 9.2
high frequency dielectric constant 5.8 - 6.2
refractive index (@1.4 μm) 2.3
transmission range 0.5 μm - 20 μm
absorption coefficient (@10.6 μm) 0.005 cm⁻¹
Phonon frequency LO (F) 31.9 meV
Phonon frequency TO (F) 26.4 meV
APPENDIX B

***************ACTONPL.BAS***************
30 REM * THIS PROGRAM SCANS THE PHOTOLUMINESCENCE
SPECTRUM OF A CRYSTAL. *
40 REM * THE USER DECIDES WHAT WAVELENGTHS TO SCAN,
AND THE DATA-TAKING *
50 REM * INTERVAL. *
60 REM * THE DATA IS PLOTTED TO THE SCREEN AND THEN
SAVED IN A FILE. *
70 REM * WRITTEN BY PAUL GILLESPIE **
80 REM **** EE/CE DEPT., RICE UNIVERSITY. MARCH/APRIL 1990.
****
90 REM ****************************************************
100 REM
110 REM GOTO 580 ' FOR TESTING DATA INPUT PART
120 REM ****************************************************
130 REM **** SETTING UP COMMUNICATIONS WITH THE DVM
*****
140 REM **** LINES 300 TO 550 ARE TAKEN FROM FLUCAP BY BILL
WILSON ****
150 REM ****************************************************
160 CR$ = CHR$(13) ' DEFINE CARRIAGE RETURN
170 CLEAR , 53152!
180 IBINIT = 53152!
190 BLOAD "bib.m", IBINIT
200 CALL IBINIT
(IBRD%,IBWRT%,IBCMD%,IBWAIT%,IBRPP%,IBONL%,IBRSC%,IBSIC%
,IBSR%,IBRXL%,IBRSV%,IBLPE%,IBPAD%,IBSAD%,IBIST%,IBDMA%
,IBEOS%,IBTMO%,IBEOT%,IBGTS%,IBCAC%,IBDIAG%,IBSTA%,IBER%
R%,IBCNT%)
210 BD%=0 ' BOARD 0 IS HP-IB
220 Dim INTENSITY(2000)
230 Dim INTEN(2000)
240 CALL IBSIC%(BD%) ' SET PC AS BUSS CONTROLLER
250 IF IBSTA% < 0 THEN STOP ' IF ERROR, THEN STOP
260 V% = 1
270 CALL IBSRE%(BD%,V%)
280 CMD$="("+CHR$(&H4) ' REMOTE ENABLE
290 CALL IBCMD%(BD%,CMD$)
300 CML$="@" ' SET LISTEN ADDRESS OF THE 8123 AS & (SEE
7470 MANUAL P 16)
310 CMT$="H" ' TALK ADDRESS IS "H" NOTE THE " " BLANK AFTER
F, WHICH IS GBIB-PC
320 CALL IBCMD%(BD%, CML$)  ' GET THE FLUKE'S
ATTENTION
330 CRS = CHR$(13)  ' DEFINE CR AS TERMINATOR
340 CM$ = " F1 R3"   ' WILL GET VOLTAGE READING FROM
VOLTOMETER
350 REM
360 REM ***** WRITING THE COMMAND TO GET THE VOLTAGE *****
370 REM ****************************
380 CMD$ = CM$ + CRS  ' ADD TERMINATOR
390 CALL IBWRIT%(BD%, CMD$)  ' WRITE THE COMMAND
400 CALL IBCMD%(BD%, CMT$)  ' PUT MACHINE IN TALK
MODE
410 REM ****************************
420 REM ****************************
430 REM ***** BEGINNING OF INTERACTIVE PROGRAM WITH USER,
TAKING DATA *****
440 REM ****************************
450 REM
460 CLS  ' CLEAR THE SCREEN
470 REM
480 REM ****************************
490 REM ***** MENU 1: INPUTTING SAMPLE ID'S, DATE, USER, ETC.
*****
500 REM ****************************
510 REM
520 CRS = CHR$(13)
530 KEY 1,"ID  1"+CR$: KEY 2,"MATERIAL  2"+CR$: KEY 3,"TEMP
3"+CR$
540 KEY 4,"DATE  4"+CR$
ON 10"+CR$
560 KEY 7,CR$: KEY 8,CR$: KEY 9,CR$
570 KEY ON
580 CLS
590 PRINT "ID:   ", SAMPLEID$
600 PRINT "MATERIAL:  ", MATERIAL$
610 PRINT "TEMP:   ", TEMP$
620 PRINT "DATE:    ", SCFDATE$
630 PRINT "OPERATOR:  ", OPR$
640 PRINT "FILE:    ", SCFILE$; PRINT
650 PRINT "TO ENTER SAMPLE ID, MATERIAL, TEMPERATURE,
DATE, OPERATOR OR"
660 PRINT "FILE TO SAVE DATA, PRESS THE APPROPRIATE SOFT
KEY."
670 INPUT CHOICE$: CHOICE = VAL(RIGHT$(CHOICE$, 1))  ' FINDS KEY #
680 ON CHOICE GOSUB 720, 730, 740, 760, 770, 780, 670, 670
690 IF CHOICE <> 0 GOTO 580
700 INPUT "DO YOU WISH TO START THE SCAN?"; ANS$
710 IF ANS$="Y" OR ANS$="y" GOTO 800 ELSE GOTO 580
720 INPUT "ENTER SAMPLE ID NAME "; SAMPLEID$ : RETURN
730 INPUT "ENTER MATERIAL NAME (I.E. ZNSE) "; MATL$: RETURN
740 INPUT "ENTER TEMPERATURE OF THE SAMPLE TO BE SCANNED (I.E.77K) "; TEMP$
750 RETURN
760 INPUT "ENTER DATE (I.E. 4/11/88) "; SCDATE$ : RETURN
770 INPUT "ENTER OPERATOR'S INITIALS "; OPR$ : RETURN
780 PRINT "ENTER FILENAME FOR DATA TO BE SAVED (I.E. ZNSE2)."
790 INPUT "DO NOT GIVE A FILE EXTENSION (I.E. .DAT). "; SCFILE$ : RETURN
800 KEY OFF
810 CLS ' CLEARS THE SCREEN
820 REM
830 REM ***** STARTING THE SCAN *****
840 REM
850 PRINT "******* HIT ANY KEY TO CONTINUE *******"
860 INPUT CONTINUE$
865 INPUT "SELECT THE DESIRED GRATING 1=2400 G/MM, 2=1200 G/MM, 3=600 G/MM";G$
870 INPUT "WHAT IS THE STARTING WAVELENGTH (IN nm) INCLUDE 1 DECIMAL": WLMIN$
880 IF LEN(WLMIN$) < 4 GOTO 870
890 OPEN "COM1:9600,N,8,1" AS #1
892 REM "CHR$(13)" IS "CR", NECESSARY FOR STATEMENT TO WORK
895 PRINT #1,CHR$(13),"NO-ECHO"
897 PRINT #1,CHR$(13),G$ + " GRATING"
900 PRINT #1,CHR$(13),WLMIN$ " GOTO"
910 INPUT "WHAT LENGTH SCAN (IN nm) WOULD YOU LIKE?"; SCANLEN
920 WLMAX = WLMIN + SCANLEN
930 INPUT "TAKE DATA EVERY HOW MANY NM? "; IDATA
940 INPUT "INPUT DELAY TIME IN SECONDS"; DEL
950 TIME = DEL*150
960 INPUT "ENTER THE MAXIMUM INTENSITY (VOLTS):(FOR SCREEN DISPLAY)"; MAXV
970 INPUT "Hit Y to take data, N to re-input data."; CONTINUE$
980 IF CONTINUE$ = "N" OR CONTINUE$="n" GOTO 810
990 CLS
1000 MX=MAXV*1000
1010 MN=-1000
1020 MX$=STR$(INT(MX))
1030 PK=VAL(MID$(MX$,1,2))
1040 K=LEN(MX$)
1050 K=K-2
1060 PR=PK*(10^K)
1070 LINE (150,50)-(600,250),6,B
1080 LINE (150,200)-(150,200)
1090 REM **** TAKING DATA POINTS ****************************
1100 REM
1110 WL$=WLMIN$
1120 LOOPCNT=SCANLEN/IDATA + 1
1130 FOR I=1 TO LOOPCNT
1140 REM **** DELAY TO STABILIZE LOCK-IN AND DVM OUTPUT
****
1150 FOR N=1 TO TIME
1160 JT=N*5
1170 NEXT N
1175 REM AVERAGES 3 DATA POINTS
1180 FOR K=1 TO 3
1190  A$ = SPACE$(60) ' STRING TO READ DVM OUTPUT
1200  CALL IBRD%(BD%,A$) ' READS VOLTAGE FROM DVM
1210  INTEN(K) = VAL (MID$(A$,1,11)) ' CONVERTS DATA TO REAL
1220 NEXT K
1230 INTENSITY(I)=(INTEN(1)+INTEN(2)+INTEN(3))/3
1240  IF INTENSITY(I) > 3.27 THEN GOTO 1280
1250  IF INTENSITY(I) < -3.27 THEN GOTO 1280
1260  INTENSITY(I) = (INTENSITY(I)*10000!)/10 ' MAKING INTENSITY AN INT
1270 GOTO 1283
1280  INTENSITY(I) = (INTENSITY(I)*1000!)/1 ' MAKING INTENSITY AN INT
1283 WLINT$ = ""
1284 WLDEC$ = ""
1285 IF I = 1 THEN WL$ = CHR$(32) + WL$
1286 REM INSERT SPACE IN FRONT OF FIRST WL$
1290 IF LEN(WL$) < 5 THEN WL$ = WL$ + CHR$(46) + "0"
1300 WLINT$ = LEFT$(WL$,4)
1310 WLDEC$ = MID$(WL$,6,1)
1320 PRINT #1,CHR$(13),WLINT$ + CHR$(46) + WLDEC$,"GOTO"
1330 REM PRINT I,WL$,WLINT$,WLDEC$,LOC(1)
1340 WL$=STR$(VAL(WLMIN$)+IDATA*I)
1350 IF LEN(WL$) < 4 THEN WL$ = WL$ + ".0"
1355 BIT$ = INPUT$(LOC(1),#1)
1360 REM SCREEN AUTOPILOT ROUTINE
1370 PT=INTENSITY(I)/1000
1380 Y=PT*200/PK
1390 Y=250-Y
1400 X=150+((I-1)*450/LOOPCNT)
1410 LINE -(X,Y),5
1420 NEXT I
1430 IF SCFILE$<>"" THEN GOTO 1460  ' FILENAME ALREADY INPUTTED?
1440 INPUT "FILE NAME (ENTER <NO> TO NOT SAVE DATA) ";
    SCFILE$
1450 IF FILE$="NO" THEN GOTO 1560  ' 1900 IS END
1460 SCFILE$="B:"+ SCFILE$ + ".DAT"
1470 OPEN SCFILE$ FOR APPEND AS #2
1480 WRITE #2, SAMPLEID$,,MATL$,,TEMP$,,SCDATE$,,OPR$
1490 WRITE #2, WLMIN, WLMAX, DATAINT
1500 WRITE #2, ";"  ' SIGNALS THE END OF A SCAN
1510 FOR I = 1 TO LOOPCNT
1520 WRITE #2, INTENSITY(I)
1530 NEXT I
1540 WRITE #2, ";"  ' SIGNALS THE END OF A SCAN
1550 CLOSE #1
1560 CLOSE #2
APPENDIX C

******************************************************************************APLOT.BAS******************************************************************************
10 REM ****  APLOT.BAS TAKES DATA FILES FROM
20 REM ****  ACTONPL.BAS AND ******
30 REM ****  VOLTS*1000) VS. WAVELENGTH (IN nm). ******
40 REM ***  WRITTEN BY PAUL GILLESPIE ******
50 REM ***  RICE UNIVERSITY, APRIL, 1988 ******
60 REM
90 REM**************************************************************************************************
100 REM****  SET-UP OF BASIC FOR IEEE-48 BOARD
**************************************************************************************************
105 REM**************************************************************************************************
110 CLEAR ,53152!
120 IBINIT = 53152!
130 BLOAD "bib.m",IBINIT
140 CALL IBINIT
(IBRD%,IBWRT%,IBCMD%,IBWAIT%,IBRPP%,IBONL%,IBRSC%,IBSIC
%,IBSRE%,IBRTL%,IBRVS%,IBLPE%,IBPAD%,IBSAD%,IBIST%,IBDMA
%,IBEOS%,IBTM0%,IBEOT%,IBGTS%,IBCAC%,IBDIAG%,IBSTA%,IBER
R%,IBCNT%)
150 BD%=0  'BOARD 0 IS HP-IB
160 CALL IBSIC%(BD%)  'SET PC AS BUSS CONTROLLER
170 IF IBSTA% < 0 THEN STOP  'IF ERROR,THEN STOP
180 V%=1
190 CALL IBSRE%(BD%,V%)  'REMOTE ENABLE
191 DIM V(4000)
193 REM  GOTO 1300  ' TO TEST PLOTTING HEADINGS
195 REM
200 REM **********END OF BASIC SET-UP FUNCTION
210 REM
500 REM ********** READ DATA FROM DISC
510 REM
511 REM ** DATA FILE IS SAMPLEID$, MATL$, TEMPS,$,
SCDATE$, OPR$, **********
512 REM ** WLMIN, WLMAX, DATAINT; INTENSITY(1) TO
513 REM ** INTENSITY(LOOPCNT)*****
514 REM
515 SPNM = 215.32  ' 215.32 STEPS PER NANOMETER
516 WAVELENGTH
517 CLS
520 INPUT "INPUT FILENAME (IE. ZNSE1, NOT ZNSE.DAT)"; SCFILE$
522 A$=SCFILE$
525 SCFILE$="B:"+SCFILE$+".DAT"
530 OPEN SCFILE$ FOR INPUT AS #1
531 INPUT #1, SAMPLEID$, MATL$, TEMP$, SCDATE$, OPR$
532 INPUT #1, WLMIN, WLMAX, DATINT
533 LOOPCNT = INT((WLMAX-WLMIN)/DATINT)
540 FOR I = 0 TO LOOPCNT
550 INPUT #1, V(I)
560 NEXT I
800 REM *********** MIN-MAX FINDING ROUTINE
810 REM
820 VMIN = 0
830 VMAX = 1
831 MN$ = STR$(INT(WLMIN)) : MINLEN=LEN(MN$)-2 'ORDER OF MAG OF WLMIN
832 MX$ = STR$(INT(WLMAX)) : MAXLEN=LEN(MX$)-2 'ORDER OF MAG OF WLMAX
840 REM XMIN = (WLMIN(10^MINLEN))*(10^MINLEN)
855 REM XMAX = (WLMAX(10^MAXLEN))*(10^MAXLEN)
856 XMIN = (INT(WLMIN/10))^10
857 XMAX = (INT(WLMAX/10))^10 + 10
860 FOR I = 1 TO LOOPCNT
870 IF V(I) < VMIN THEN VMIN = V(I)
880 IF V(I) > VMAX THEN VMAX = V(I)
890 NEXT I
900 REM *********** END OF MIN-MAX FINDING ROUTINE
910 REM
1000 REM ********** HP7470 PLOTTING ROUTINE
1100 REM
1200 VMAX% = ((VMAX*1000) + 1)*1000
1210 VMAX$ = STR$(VMAX%)
1220 VMIN% = ((VMIN*1000) - 1)*1000
1230 VMIN$ = STR$(VMIN%)
1240 XMIN$ = STR$(XMIN)
1250 XMAX$ = STR$(XMAX)
1300 CMD$ = "%"+CHR$(&H4) 'RESET THE 7470;"%" IS THE LISTEN ADDRESS
1310 CALL IBWRT%(BD%, CMD$)
1320 CML$ = "@%" 'SET LISTEN ADDRESS(SEE 7470 MANUAL P 16)
1330 CMT$ = "?E" 'TALK ADDRESS IS "E"
1340 CALL IBCMD%(BD%, CML$) 'GET THE 7470'S ATTENTION
1350 CR$ = CHR$(3) 'DEFINE ETX AS TERMINATOR
1360 CMS$ = "IN;SP1" 'INITIALIZE, SELECT PEN 1
1370 GOSUB 2500
1400 CMS$="PU;PA 2370,7200;SI .25,.5" : GOSUB 2500
1405 CMS$="LB INTENSITY VS. WAVELENGTH" + CR$ : GOSUB 2500
1410 CMS$="PU;PA 7000,6400;SI;LB SAMPLE: "+SAMPLEID$+CR$
1415 GOSUB 2500
1420 CM$="PU;PA 7000,6200;SI;LB MATERIAL: "+MATL$+CR$+
1425 GOSUB 2500
1430 CM$="PU;PA 7000,6000;SI;LB TEMPERATURE:"+TEMP$+CR$+
1435 GOSUB 2500
1436 CM$="PU;PA 7000,5800;SI;LB FILENAME: "+A$+CR$+
1437 GOSUB 2500
1440 CM$="PU;PA 7000,5600;SI;LB DATE RUN: "+SCDATE$+CR$+
1445 GOSUB 2500
1450 CM$="PU;PA 7000,5400;SI;LB OPERATOR: "+OPR$+CR$+
1455 GOSUB 2500
1460 CM$="PU; PA 4000, 200;SI;LB WAVELENGTH (nm)" + CR$+
1465 GOSUB 2500
1470 CM$="PU; PA 150, 3000;DR 0, 1;LB VOLTS*1000"+CR$+
1475 GOSUB 2500
1480 CM$ = "IN;SP2"  'INITIALIZE, SELECT PEN 2
1490 GOSUB 2500
1500 CM$ = "IP 700,750,9600,7500" 'DEFINE BOUNDARIES
1510 GOSUB 2500
1520 CM$ = "SC"+XMIN$+,"+XMAX$+,"+VMIN$+,"+VMAX$ 'SCALE
1530 GOSUB 2500
1540 CM$ = "PU"+XMIN$+,"+VMIN$+;"+VMIN$+;"
1550 GOSUB 2500
1560 CM$ = "PD"+XMAX$+,"+VMIN$+;"+VMIN$+;"+VMAX$+;"+VMAX$+;"+VMAX$+;"+VMAX$+;"+VMAX$+;"
1570 GOSUB 2500
1580 CM$ = XMIN$+,"+VMIN$+"PU;SP1"
1590 GOSUB 2500
1600 PRINT "THE PLOT WILL GO FROM " XMIN " TO " XMAX " nm."
1610 INPUT "LABEL EVERY HOW MANY nm?"; XLBLINT  ' DO FOR VOLTS, TOO?
1620 FOR X = XMIN TO XMAX STEP XLBLINT  'LABEL X AXIS
1630 CM$ = "PA"+STR$(X)+";"+VMIN$+";XT";GOSUB 2500
1640 CM$ = "CP-1.5,-1;LB"+STR$(X)+CR$;GOSUB 2500
1650 NEXT X
1660 FOR Y = VMIN% TO VMAX% STEP 1000  'LABEL Y AXIS
1670 CM$ = "PA"+XMIN$+";"+STR$(Y)+";YT";GOSUB 2500
1680 CM$ = "CP-6,-.25;LB"+STR$(Y)+CR$;GOSUB 2500
1690 NEXT Y
1700 REM *********** START PLOTTING DATA
1710 REM
1720 REM *** S IS THE WAVELENGTH IN nm BETWEEN DATA
1730 S = (DATAINT)
1740 X = WLMIN
1750 CM$ = "PU;PA"+STR$(X)+";"+STR$(V(1))+";PD";GOSUB 2500
1760 FOR K = 2 TO (LOOPCNT)
1770 X = WMIN + ((K-1)*S)
1780 CM$ = "PA"+STR$(X)+","+STR$(V(K))':GOSUB 2500
1790 NEXT K
1800 REM CM$="SC;PU;PA 2400,7000;SI .25,.5;LB PL SPECTRA"
   FOR"+A$+CR$+
2400 CM$ = "SP0;"
2405 GOSUB 2500
2410 CLS
2415 PRINT "PLOT IS COMPLETE"
2420 END
2500 CALL IBWRT%(BD%,CM$)
2510 RETURN
2400 C