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Laser-assisted metalorganic chemical vapor deposition of zinc selenide

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Rice University, 1992
RICE UNIVERSITY

LASER-ASSISTED METALORGANIC CHEMICAL VAPOR DEPOSITION OF ZINC SELENIDE

by

GREGORY B. SHINN

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

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ABSTRACT

Laser-Assisted Metalorganic Chemical Vapor Deposition of Zinc Selenide

by

Gregory B. Shinn

Laser-assisted metalorganic chemical vapor deposition (LMOCVD) has been used to grow epitaxial zinc selenide at temperatures as low as 200 °C. The metalorganic sources, dimethylzinc (DMZ) and diethylselenide (DESe), were photodissociated with radiation from a 193 nm ArF excimer laser passing parallel to a (100) GaAs substrate. A two-stage purge scheme prevented deposition on the windows while minimizing disturbances to the gas flow in the growth region. The temperature dependence for both thermal and laser-assisted film growth was examined, keeping other reaction parameters fixed. The laser-assisted growth rate of ZnSe remained approximately constant at 1 µm/h over the temperature range 200-400 °C, temperatures at which no thermal growth occurs. At higher temperatures the thermally driven process was important and dominated the growth at temperatures above 500 °C.

Photoluminescence analysis indicated that material grown at 400 °C by the laser-assisted process was of better quality than films grown by either method at other temperatures.

The effects of laser energy density and repetition rate on growth rate were examined. The growth rate at 20 Hz increased from 1.1 µm/h at 15 mJ per pulse laser energy to 2.5 µm/h with a 48 mJ pulse energy with all other reactor
conditions kept constant. Above a pulse energy of 40 mJ, the LMOCVD growth rates reached maximum values of about 2.7 μm/h and 4.6 μm/h for 20 Hz and 40 Hz operation, respectively. The rate was approximately doubled when the laser repetition rate was increased from 20 Hz to 40 Hz.

A two-level design of experiments matrix was done to examine the effect of six reactor parameters on film growth rate. Increases in substrate temperature, dimethylzinc partial pressure, diethylselenide to dimethylzinc source ratio and use of the laser all resulted in higher growth rate while increased reactor pressure was found to decrease the film growth rate.

A film grown with the laser radiation incident to the growth surface at a laser energy density of approximately 5 mJ/cm² exhibited the highest donor-bound exciton to self-activated center luminescence ratio of all films grown during this study.
ACKNOWLEDGEMENTS

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Thank you to my wife Victoria and daughter Carolyn who have given me many happy hours to offset time spent in the lab and at work.

The author dedicates this work to his parents, Dennis and Sherry Shinn, without whose encouragement and advice this work may never have been completed.
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<td>ALE</td>
<td>atomic-layer epitaxy</td>
</tr>
<tr>
<td>amu</td>
<td>atomic mass unit</td>
</tr>
<tr>
<td>DESe</td>
<td>diethylselenide</td>
</tr>
<tr>
<td>DEZ</td>
<td>diethylzinc</td>
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<tr>
<td>DIP</td>
<td>dual in-line package</td>
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<td>DMCd</td>
<td>dimethylcadmium</td>
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<td>DMSe</td>
<td>dimethylselenide</td>
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<td>dimethyltelluride</td>
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<td>DMZ</td>
<td>dimethylzinc</td>
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<td>LEED</td>
<td>low-energy electron diffraction</td>
</tr>
<tr>
<td>LMOCVD</td>
<td>laser-assisted metalorganic chemical vapor deposition</td>
</tr>
<tr>
<td>LPE</td>
<td>liquid-phase epitaxy</td>
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<tr>
<td>MBE</td>
<td>molecular-beam epitaxy</td>
</tr>
<tr>
<td>MOCVD</td>
<td>metalorganic chemical vapor deposition</td>
</tr>
<tr>
<td>MOVPE</td>
<td>metalorganic vapor-phase epitaxy</td>
</tr>
<tr>
<td>OMVPE</td>
<td>organometallic vapor-phase epitaxy</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>RHEED</td>
<td>reflection high-energy electron diffraction</td>
</tr>
<tr>
<td>TMG</td>
<td>trimethylgallium</td>
</tr>
<tr>
<td>TRR</td>
<td>time-resolved reflectivity</td>
</tr>
<tr>
<td>TTL</td>
<td>transistor to transistor logic</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra-high vacuum</td>
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<td>VPE</td>
<td>vapor-phase epitaxy</td>
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Chapter 1
Introduction

Zinc selenide is a II-VI compound semiconductor with a direct band gap of 2.67 eV at room temperature. It has received considerable attention in recent years as a potentially useful material for blue optoelectronic devices. Difficulties in the control of electrical properties, and in particular in obtaining low-resistivity p-type material, has limited the use of ZnSe for optoelectronic applications. Progress in obtaining high quality ZnSe epitaxial films has been made using low-temperature molecular-beam epitaxy (MBE) (1, 2, 3) and low-temperature, low-pressure metalorganic chemical vapor deposition (MOCVD). (4, 5) In fact, several researchers have reported p-type conduction in ZnSe heterolayers grown by MBE (6, 7) and MOCVD. (5, 8) Ren et al. (9) fabricated a ZnSe p-n junction diode by MBE using Li and Cl as substitutional dopants. One important aspect of material preparation by MBE or MOCVD is the low growth temperature. The better quality films have been deposited at temperatures below about 350 °C to control crystal defects and minimize incorporation of impurities.

Photo- or laser-assisted MOCVD is a technique that has been successful in attaining low-temperature growth of both II-VI and III-V compound semiconductors. (10, 11) This technique uses ultraviolet radiation rather than thermal energy to dissociate the metalorganic chemical bonds. Many of the metal alkyls used in MOCVD have broad absorption spectra in the wavelength region below approximately 250 nm. Low-pressure mercury lamps, as well as excimer lasers at either 193 nm or 248 nm, have been used to photodissociate
the source gases. GaAs (12, 13), InP (14, 15), CdTe (16, 17), HgTe (18, 19), Cd$_x$Hg$_{1-x}$Te (19, 20), ZnS (18), and ZnSe (21, 22), and ZnS (18) have all been grown using photo-assisted epitaxy. Work presented in this thesis is the first laser-assisted MOCVD growth of ZnSe epitaxial films.

The goal of this work was to construct a working reactor system and demonstrate the laser-assisted MOCVD of ZnSe. Using the low-temperature growth capabilities of this system, future researchers would use this system for studies on controlled doping of high quality ZnSe epitaxial films. A laboratory reaction system was designed and built in the time period from 1986 to 1988 and laser-assisted MOCVD grown ZnSe films were successfully deposited on (100) GaAs substrates. The bulk of the experimental work presented here was done over the period from August 1988 to May 1989.

The experimental MOCVD reactor system was a stainless-steel, horizontal, cold-wall reactor, with provisions for resistively heating the substrate. There were six major subsystems in the overall MOCVD system. These were i) the hydrogen carrier gas purification and flow rate control, ii) the metalorganic bubbler transport systems, iii) the reactor, iv) the exhaust system with a pyrolysis furnace, particle filters and vacuum pump, v) the system control electronics and interlocks, and vi) the excimer laser and necessary optics. A detailed description of the MOCVD system is contained in Chapter 4.

Laser-assisted ZnSe film growth was successfully demonstrated in the experimental reactor system. Experiments to examine the effect of temperature, several laser parameters, source gas flow rates, and pressure on film deposition rate and quality were performed. It was found that the LMOCVD growth rate was nearly independent of temperature over the wide temperature
range from about 400 °C down to 200 °C. Presentation and discussion of these results is given in Chapter 6. Chapter 5 contains a detailed description of the experimental procedures and film characterization techniques used during these experiments.

Chapter 2 of this thesis gives a brief overview of ZnSe epitaxial growth techniques with some overview of previous work in ZnSe MOCVD. A section on substrate material considerations is included because of the importance of the choice of substrate material in epitaxial growth. Chapter 3 contains data on the crystallographic, thermal, electrical, optical and thermodynamic properties of ZnSe for reference.
Chapter 2
Zinc Selenide Epitaxy

In this work ZnSe heteroepitaxial films have been grown on GaAs by laser-assisted and conventional metalorganic chemical vapor deposition (MOCVD). Information in the following chapter is included to help understand why this particular growth technique and heteroepitaxial system were chosen. There are several epitaxial techniques by which ZnSe thin films can be grown. Section 2.1 contains a brief description of some of those techniques and discussions of the their relative advantages and disadvantages for production of ZnSe epilayers. A brief overview of the literature on ZnSe MOCVD growth is given in section 2.2, followed by a review of photo-assisted MOCVD of compound semiconductors in section 2.3. This section also contains information from the literature about the ultraviolet absorption spectra of metalorganic compounds typically used in MOCVD. Finally, substrate material issues are discussed in section 2.4.

2.1 Epitaxial Techniques

2.1.1 Liquid-Phase Epitaxy

Liquid-phase epitaxy (LPE) is somewhat similar to bulk crystal growth from seeded solutions in that epitaxial layers are grown from molten solutions in contact with a seed crystal. Metals such as Bi, Zn, and Zn-Ga or Zn-Sn alloys or metal halides such as ZnCl₂ have been used as solvents for ZnSe in LPE. (23)
Growth temperatures from the metallic melts are in the range from 800 °C to 1080 °C whereas growth from the halide melt can take place at temperatures of 700 °C or less. The process can be carried out by several growth techniques (24), but in general the LPE technique consists of a temperature ramp up to and stabilization at the melt temperature for the solvent and ZnSe powder at which time the substrate is contacted with the melt. Initially there is a melt back of the substrate surface and formation of the solute boundary layer. Then the melt temperature is slowly lowered at a rate of several °C/min or less to attain supersaturation of the solute in the melt and onset of film growth. The substrate is separated from the melt after a period of time to stop the process when the desired thickness is reached.

LPE is a simple technique to apply and results in films with good purity. However, LPE of multilayer structures with well controlled interfaces is difficult and the thickness uniformity of LPE grown films is usually poor relative to other techniques. (25)

2.1.2 Vapor-Phase Epitaxy

Vapor-phase epitaxy (VPE) is the growth of material from gaseous sources where one or both of the elements are introduced to the growth region using halide transport. Stucheli and Bucher (26) used VPE for ZnSe epitaxy on GaAs. Iodine was used to transport Zn to the substrate. Hydrogen carrier gas flowed through the iodine source to transport iodine into the ZnSe source region (which is heated to 800 °C) where the iodine reacted with Zn to form ZnI2. Selenium was transported as Se vapor or reacted with H2 to form H2Se.
The gaseous products from the source zone are transported to the substrate in H₂ carrier gas. The temperature gradually decreased from outside the source zone to the substrate so that at the typical growth temperatures in the range of 600 °C to 650 °C supersaturation of the source materials was attained. Zinc iodide reacted with selenium in the lower temperature zone to form epitaxial ZnSe films at a rate of about 0.5 μm/h.

The advantages of VPE are the high transport rates of source material to the substrate for good throughput of material and the relatively low growth temperature compared to LPE. Doping can be easily done by addition of a gaseous dopant to the reactor. But, the process is not well suited for multilayer structures such as superlattices since it is necessary to transport the substrate between reactors to obtain alternating layers of different materials. And although the growth temperature is low compared to that for LPE it is high compared to that for MBE or MOCVD.

2.1.3 Molecular-Beam Epitaxy

Molecular-beam epitaxy (MBE) is a relatively simple process that involves the vacuum evaporation of elemental sources onto a heated substrate. Controlled fluxes of Zn and Se onto the substrate are attained using temperature-controlled sources called Knudsen cells. The source materials are directed at the substrate through cooled beam collimators and the growth turned on and off using shutters. The epitaxial growth rate is slow, but very well controlled. Because of the ultra-high vacuum environment, in situ monitoring of crystal structure and impurity concentrations are possible using techniques
such as low energy electron diffraction (LEED) and Auger electron spectroscopy. The technique is very well suited for abrupt interface control in the fabrication of superlattice structures.

Although high quality epitaxial material can be deposited using MBE, the technique has several disadvantages for production. The low growth rate that allows epitaxial growth at low temperatures also leads to low throughput for the single-wafer process. Capital costs for the UHV system and diagnostics are high. Finally, operating expenses to maintain a UHV environment can be high and maintenance requirements can lead to long shutdowns for bakeout of the equipment.

2.1.4 Atomic-Layer Epitaxy

Atomic-layer epitaxy (ALE) is actually one particular method of MBE. Whereas the typical MBE process involves the concurrent flux of both ion species to the substrate, in ALE only one element is allowed to impinge on the surface at a time. For instance, in the case of ZnSe the process involves cycling between Zn and Se ion fluxes, growing one full atomic monolayer during each part of the cycle. It is thought that any excess atoms are reevaporated from the surface once a full monolayer is grown. Experimental observation of the RHEED (reflection high energy electron diffraction) beam pattern intensity during ALE supports this assumption. Yao et al. (27) monitored the temporal response of the RHEED beam intensity during the ALE of ZnSe. They observed that the beam intensity saturated when the surface was covered with an adsorbed Zn monolayer. The intensity did not change with further Zn beam flux, but was reduced and eventually saturated at a lower level when the Se flux was
introduced. When the Zn beam was turned on again, the beam intensity increased and saturated at the same level as the previous Zn-covered surface. Extremely good thickness control should be achievable with this monolayer-by-monolayer technique since the growth rate is directly proportional to the number of flux cycles.

There are several distinct advantages to ALE over other epitaxy techniques. First is the monolayer-by-monolayer control of film growth. Cornelissen et al. (28) used ALE to grow ZnSe/ZnS\(_{0.2}\)Se\(_{0.8}\) superlattices that appear to be more atomically smooth than those grown by MBE. Not only does this give thickness control down to atomic layers in the crystal lattice, it may also allow controlled doping of the layers by selective choice of the available lattice sites during incorporation of the dopant. Good quality epitaxy may also be possible at growth temperatures even lower than MBE.

ALE has the same disadvantages for mass production as MBE, namely low throughput and high capital and operational costs. Also, the film growth rate is about an order of magnitude lower than that for MBE. (28) This may result in higher impurity concentrations since the total amount of impurities outgassing from the chamber walls during film growth will be increased because of the longer deposition time.

### 2.1.5 Metalorganic Chemical Vapor Deposition

Metalorganic chemical vapor deposition (MOCVD) is also referred to as metalorganic vapor-phase epitaxy (MOVPE) or organometallic vapor-phase epitaxy (OMVPE). MOCVD is similar to halide-transport VPE in that molecular
species are used to carry the source elements to the growth region at high transport rates. As the name implies, these source molecules are metalorganic compounds such as dimethylzinc and diethylselenide. These materials are available as high purity liquid sources and are typically introduced into the growth chamber by bubbling a carrier gas such as hydrogen through a bubbler containing the metalorganic compound. (see section 4.3) Unlike VPE, MOCVD is a cold wall process. The substrate is the hottest location in the reactor. The sources are transported to the region near the substrate where they react to form the epitaxial film.

The substrate is typically heated from 350 °C to 750 °C, depending on the source gases and reactor conditions. Film growth occurs at the lower temperatures when hydrogen selenide is reacted with zinc metalorganic sources, but growth temperatures of 450 °C or greater are required to obtain appreciable growth rates when both sources are metalorganic. ZnSe film growth rates of 1 μm/h or more have been obtained by MOCVD.

MOCVD, when compared to the other epitaxial techniques, is well suited for production. The typical film growth rate for batch silicon epitaxy as used in production is two to three μm/h for 150 mm wafers. The fast growth rates for MOCVD processes mean that high throughput is possible. Films of high purity can be grown and abrupt multilayer structures can be grown through use of fast switching gas manifolds. However, there are some problems or disadvantages as with all the other techniques. Stringent safety precautions must be maintained if toxic materials such as hydrogen selenide are used and care is needed to deal with any unreacted pyrophoric materials such as the metalorganic sources. Metalorganic source materials are quite expensive,
leading to relatively high operating costs. Finally, pre-reaction of the source materials in the gas phase must be avoided by careful choice of reactor design or source material and precise control of the growth parameters so that high quality material can be obtained.

2.2 ZnSe MOCVD - Historical Overview

Manasevit and Simpson (29, 30) were the first to report the deposition of II-VI compounds from metalorganic sources. They reacted \((\text{C}_2\text{H}_5)_2\text{Zn} \) (DEZ) and \((\text{CH}_3)_2\text{Cd} \) (DMCd) with \(\text{H}_2\text{Se}, \text{H}_2\text{S}\) or \((\text{CH}_3)_2\text{Te} \) (DMTe) at atmospheric pressure in hydrogen carrier gas. The optimum temperature for ZnSe epitaxial growth on several oriented oxide substrates was between 725 °C and 750 °C. They observed rough surface morphology for these films, a problem most likely caused by the inclusion of particles formed in gas-phase reactions.(31)

Stutius (31) and Blanconnier et al. (32) realized that the instability of the cation metalorganic molecule and \(\text{H}_2\text{Se}\) led to excessive homogeneous gas-phase reactions that resulted in poor film quality. The instability is so severe that the gas phase reactions can occur even at room temperature. Stutius took three actions to minimize premature gas-phase reactions. First, he determined that the premature reactions were less likely with \((\text{CH}_3)_2\text{Zn} \) (DMZ) than with DEZ. He attributed this result to the relative strengths of the Zn-C bonds. Therefore he used only DMZ for the Zn source in his work. Second, he introduced the reactants into the reactor through separate injectors, mixing them in the vicinity of the substrate. Finally, he minimized the probability for gas phase collisions by operating at lower pressures near 0.15 torr. Blanconnier et al. also designed their reactor so the reactants were mixed close to the
substrate surface, but used the strategy of heavily diluting the reactants with H₂ carrier gas to reduce the probability of gas phase reactions.

Stutius (31) realized the importance of substrate choice on film quality. The growth morphology and photoluminescence properties of ZnSe films deposited on (100) GaAs were superior to those properties for films deposited on (111) GaAs or (0001) sapphire substrates. Single-crystal ZnSe layers were deposited on (100) GaAs at 350 °C and 0.15 torr using a Se/Zn source ratio of 5 to 1. The effects of the substrate material and orientation are discussed in more detail in section 2.4.

Premature reaction problems can be avoided by using more stable reactants, in particular by using an alternative Se source. It is also desirable to replace H₂Se with an alternative source since it is extremely toxic like the Group V hydrides. Wright et al. (33) deposited ZnS, ZnSe and ZnO from DMZ and several heterocyclic compounds. ZnSe was deposited at atmospheric pressure from selenophene (C₄H₄Se) and DMZ, and rates of approximately 0.6 μm/h were achieved in the temperature range between 550 °C and 600 °C. There was no evidence of premature reactions and the optical transmittance and morphology of the films were comparable to those for films grown using H₂Se.

Another alternative is to use both zinc and selenium metalorganic molecules. The deposition temperature needs to be higher than for H₂Se reactions, and therefore could lead to a higher concentration of native defects, but premature gas phase reaction problems are eliminated. Mitsuhashi et al. (34) examined MOCVD ZnSe growth from all combinations of the dimethyl and diethyl zinc and selenium sources. Epitaxial ZnSe films were grown on (100) GaAs substrates at 300 torr. Several important observations were made about
the growth rate data. Above 500 °C, film growth rate was independent of
temperature, indicating a mass transport limited process. At lower temperatures
the growth rate is kinetically controlled. Interestingly, the apparent activation
energy for all combinations of reactants is the same (22-24 kcal/mol), a fact that
may indicate the formation of a common intermediate species that controls the
growth process. Under growth conditions of excess Se source, the growth rate
increases with increasing Se flow, but is independent of Zn source flow rate.
These observations point to a growth process limited by a surface process
involving the Se source. However, the growth process may be more
complicated. Giapis et al. (35) found that the apparent activation energy for the
DMZ/DES¢ reaction is pressure dependent, which indicates that the growth
process is complex and may involve both gas-phase and surface processes.

High quality material has been grown using metal alkyls for both sources.
Yasuda et al.(8) successfully grew low-resistivity p-type ZnSe on GaAs from
DMZ and DES¢ with lithium nitride dopant. The substrate growth temperature
was 450 °C and reactor pressure either 300 or 760 torr. ZnSe films on the order
of 1 μm thick exhibited p-type conductivity with high mobility (∼40 cm²/Vs) and
carry concentration (9 x 10¹⁷ cm⁻³). N-type ZnSe was deposited on top of the
p-type material to form ZnSe p-n diodes that exhibited blue emission near 467
nm.

2.3 Photo-Assisted Epitaxy

Photo-assisted growth of compound semiconductors is one technique
which has been used to obtain a low temperature growth environment during
Epitaxy. Ultraviolet radiation from a low-pressure mercury lamp with strong emission at 253.7 nm and 184.9 nm has been used to photodissociate the metal alkyls often used as source materials in metalorganic chemical vapor deposition (MOCVD). Epitaxial films of GaAs (13), HgTe (36), CdTe (16), ZnSe (21), and Cd$_x$H$_{1-x}$Te (19) have been grown in this manner. ZnSe films were grown on (100) GaAs and glass substrates using a low-pressure mercury lamp to photodissociate diethylzinc and dimethylselenide. (21) Photo-enhanced growth was observed at temperatures as low as 200 °C.

Epitaxial films of compound semiconductors have also been grown using UV and visible lasers acting as either a localized heating source for pyrolytic growth or as a source of UV photons to drive photolytic processes. The photo-assisted growth of GaAs (12, 37, 38) and InP (14, 15) have been studied extensively, while some work has also been published on the laser-assisted growth of HgTe (18), Hg$_x$Cd$_{1-x}$Te (20)(18), ZnO (39), and ZnS (18).

There are three basic processes by which photo-assisted deposition of a material occurs: pyrolysis, photocatalysis, and photolysis. Laser-assisted pyrolytic deposition is an extension of conventional thermal CVD or MOCVD in which localized heating of the substrate occurs by absorption of the laser light. A laser beam at a wavelength that is absorbed by the substrate, but not the gaseous species, is focused onto the growth surface where it is absorbed causing heating of the irradiated area. The surface temperature profile and maximum surface temperature achieved during laser pyrolytic film growth depends strongly on the laser power, the optical and thermal properties of both the substrate and the film, and on the relative size of the irradiated area compared to substrate area.
Zinc has been deposited from dimethylzinc (DMZ) onto GaAs substrates with 520.8 - 568.2 nm radiation by using a cw krypton laser for substrate heating. (40) Deposition was achieved with laser powers from 65 to 190 mW which resulted in heating to maximum temperatures from 215 °C to 635 °C. Direct writing of GaAs epitaxial layers (from trimethylgallium (TMG) and arsine) was achieved using a focused argon ion laser beam in a photo-assisted atomic layer epitaxy growth technique. (38) The laser was scanned over the surface only during the time that TMG was flowing, and growth was achieved at substrate temperatures as low as 300 °C. The growth enhancement at these low temperatures could either be due to pyrolytic heating of the surface or to a photocatalytic effect where TMG is catalytically decomposed by surface reactions on the GaAs substrate or thin film.

ZnSe epitaxial films on GaAs substrates have been grown at room temperature using xenon-lamp radiation and diethylzinc and diethylselenide source materials. Growth rate enhancement was observed when the growth surface was directly irradiated. No enhancement was observed when only the gas phase was irradiated using horizontal illumination. (41) Similar growth enhancement was observed using dimethylzinc and dimethylselenide as the source materials. (42) Growth was enhanced only when the photon energy of the incident radiation was greater than the bandgap of ZnSe, significantly below the absorption band of the reactants. Surface heating was not thought to be significant since a low power density of incident light was used. It is possible that the excess electron-hole pairs in the ZnSe film generated by the absorbed radiation helped to catalytically drive some surface reactions and enhance growth.
Photochemical deposition differs from either pyrolytic or photocatalytic deposition in that the radiation is absorbed by either the gas-phase, adsorbed-layer species, or both. The laser energy is used to photodissociate reactants directly, which causes a supersaturation of the metal species in the vapor and condensation onto the nearby substrate. The laser beam can be oriented for either perpendicular irradiation of the substrate or parallel irradiation of only the gas phase above the surface. The metal alkyls often used for MOCVD have relatively broad absorption spectra in the UV below 250 nm. (43) Therefore, the radiation from low pressure mercury lamps (184.9 nm and 253.7 nm) and from excimer lasers (193 nm and 248 nm) has been used for the photochemical growth of epitaxial films. Morris (20) successfully grew mercury cadmium telluride on CdTe substrates at 150 °C using an ArF excimer laser to photodissociate dimethylmercury, dimethylcadmium and dimethyltelluride. The laser beam did not impinge on the substrate, but passed parallel to and below the growth region. Zinck et al. (17) also used a parallel irradiation scheme to attain low temperature growth of CdTe on GaAs using a 248 nm KrF excimer laser to photodissociate dimethylcadmium and diethyltelluride. In fact, an adverse effect on film uniformity was found for growth under perpendicular irradiation.

Other researchers have determined that perpendicular irradiation is beneficial to photochemical epitaxy. Irvine et al. (19) found that illumination of the substrate surface is essential for good quality HgTe and Cd$_x$Hg$_{1-x}$Te epitaxy using a low-pressure mercury lamp. Photosensitization of adsorbed Hg atoms was required to enhance surface reactions with diethyltelluride and to minimize gas phase nucleation. Donnelly et al. (15) also found perpendicular irradiation
beneficial for InP thin film growth. The growth process for InP appeared to involve the gas phase decomposition of trimethylindium and trimethylphosphine, by ArF excimer laser radiation, to InP and carbon fragments. Carbon is electrically active in III-V compound semiconductors and is therefore an unwanted impurity. The amount of carbon incorporation was minimized through desorption under subsequent laser illumination.

Surface selective growth of Zn from DMZ has been achieved using a 257 nm beam from a frequency doubled argon ion laser. Gas phase DMZ does not absorb light at 257 nm. However, the surface adsorbed species have an absorption spectrum with a tail at the long wavelength edge and do absorb light at 257 nm. Photochemical deposition of Zn was achieved at room temperature using a focused Ar+ laser and unfocused 248 nm KrF excimer laser radiation. (44)

Knowledge of the ultraviolet absorption spectra of the zinc and selenium alkyls is necessary in order to choose the best photoexcitation source. Chen and Osgood (43) measured the absorption cross sections of dimethylzinc, dimethylcadmium and dimethylmercury from 300 to 175 nm under various gas temperatures and pressures. Structured continua were observed for all three metalorganics and the absorption cross-section was found to be independent of pressure. Dimethylzinc was observed to have a maximum absorption cross-section value of $0.412 \times 10^{-16}$ cm$^2$ at 202.1 nm. Fujita et al. (4) also measured the ultraviolet absorption spectra of some group II and group VI alkyls, and obtained results similar to those of Chen and Osgood for dimethylzinc and dimethylcadmium. Measurements were made only at one gas temperature and pressure over the spectral range from 190 to 400 nm. Figure 2.3.1 contains the
ultraviolet absorption spectra of the zinc and selenium alkyls measured by Fujita et al. The maximum absorption cross section for dimethylzinc measured in this study is approximately $0.3 \times 10^{-16}$ cm$^2$. For excimer laser-induced photolysis we are interested in the absorption cross-sections of the metal alkyls at 193 nm and 248 nm, the ArF and KrF excimer laser wavelengths respectively. The absorption cross section values determined by Fujita et al. for a number of metal alkyls are listed in Table 2.3.1. Note that the absorption cross section of

![Absorption Spectrum](image)

**Figure 2.3.1** Ultraviolet absorption spectra of the zinc and selenium alkyls (18)

the metal alkyls is greater at 193 nm than at 248 nm. Indeed, with the exception of diethylzinc, the absorption at 248 nm by the gaseous zinc and selenium
alkyls is negligible. Dimethylzinc and diethylselenide have comparable absorption cross sections of approximately $0.18 \times 10^{-16} \text{ cm}^2$ at 193 nm.

Dimethylzinc is photodissociated in a single photon process by 193 nm radiation. Chen and Osgood have developed an analytic theory for the photodissociation of linear symmetric poly-atomic molecules. (45)

Table 2.3.1 Absorption cross sections of II-VI metalorganic compounds at 193 nm and 248 nm. ($x \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$) (18)

<table>
<thead>
<tr>
<th>Compound</th>
<th>193 nm</th>
<th>248 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(CH$_3$)$_2$</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Te(CH$_3$)$_2$</td>
<td>2.8</td>
<td>3.6</td>
</tr>
<tr>
<td>Te(C$_2$H$_5$)$_2$</td>
<td>4.8</td>
<td>3.6</td>
</tr>
<tr>
<td>Zn(CH$_3$)$_2$</td>
<td>1.8</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S(CH$_3$)$_2$</td>
<td>0.6</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>S(C$_2$H$_5$)$_2$</td>
<td>1.1</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Se(CH$_3$)$_2$</td>
<td>1.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Se(C$_2$H$_5$)$_2$</td>
<td>1.9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Their analysis indicates that a single 193 nm photon is sufficient to dissociate dimethylzinc into atomic zinc and two methyl radicals. The absorption of one photon breaks one zinc - carbon bond forming a monomethyl molecule and a methyl radical. Due to the small binding energy of monomethyl molecules, this molecule immediately dissociates further to a metal atom and another methyl radical.
Yu et al. have observed fluorescence from excited state zinc atoms during the photodissociation of dimethylzinc using a KrF excimer laser. (46) The fluorescence intensity had a quadratic dependence on laser intensity. This indicated that a two photon process was required for the production of the excited metal atom. Experimental evidence has shown that the excitation does not occur through excitation of the ground state metal atom, but must instead be from a two-photon photodissociation. However, the photodissociation due to two photon processes is negligible compared to single photon processes.

A surface controlled growth process may be beneficial to film quality. Therefore, it is important to know the ultraviolet absorption spectra for adsorbed molecules. Ehrlich and Osgood (47) studied the photodissociation of dimethylcadmium and trimethylaluminum on silicon dioxide. The absorption spectra for both species were red-shifted for the adsorbed molecules relative to the gas. Aluminum films were grown in a surface-controlled process using 257.2 nm radiation from a frequency-doubled argon-ion laser since gas phase absorption was minimal at this wavelength. Dimethylzinc has a similar red shift and has been successfully deposited on GaAs at low temperatures by photo-enhanced CVD using a low-pressure mercury lamp. (44)

Low temperature film growth is possible with the use of ultraviolet energy to photodissociate reactants. The metalorganic compounds used in MOCVD have high absorption cross-sections in the spectral range below 250 nm, and are known to dissociate in a single-photon process under 193 nm radiation. Diethylselenide and dimethylzinc were chosen as the sources for laser-assisted MOCVD of ZnSe in this study because of their high absorption at ultraviolet wavelengths and their availability from commercial vendors.
2.4 Description of MOCVD and Photo-assisted MOCVD Processes

The MOCVD growth process is heterogeneous, involving reactions between the gas phase reactants and the solid-phase substrate on which epitaxy occurs. The typical heterogeneous process can be described as a series of steps:

i) diffusion of reactants through a boundary layer to the surface
ii) adsorption of reactants on the surface
iii) surface reaction and/or surface motion and lattice incorporation
iv) desorption of products from the surface
v) diffusion of products through the boundary layer into the gas stream

These steps occur sequentially, the slowest step limiting the growth process. At high temperatures, the surface processes are very fast and the mass transport steps control the growth rate, leading to a growth rate that is essentially independent of temperature. At lower temperatures surface processes are usually the rate limiting steps, and the growth rate is strongly temperature dependent.

The exact mechanism for MOCVD growth of compound semiconductors is not known. The stability of the metalorganic sources determines whether they will decompose homogeneously in the gas phase at elevated temperatures or diffuse to the surface where they are adsorbed and undergo subsequent decomposition and reaction. Stable molecules are likely to remain intact until they are able to diffuse to the surface and react, whereas less stable molecules may undergo gas phase pyrolysis with by-products diffusing to the surface. The III-V systems have been more thoroughly investigated than II-VI MOCVD
systems. Kinetic studies have been made on the growth of GaAs from trimethylgallium (TMGa) and arsine (AsH₃). These compounds are relatively stable, with thermal decomposition of TMGa occurring only at temperatures above 400 °C. The results from several studies indicate that surface interactions between the reactants are important during film growth. (48)

The zinc metal alkyls are not as stable as the III-V source compounds and undergo homogeneous decomposition at temperatures between 250 °C and 300 °C. Therefore, it is plausible that they could undergo homogeneous decomposition during MOCVD growth processes. Mitsuhashi et al. (36) investigated the kinetics of ZnSe MOCVD growth from a number of zinc and selenium alkyls. Based on their experimental results, they proposed a four step mechanism for ZnSe MOCVD.

i) the zinc alkyl decomposes into zinc and alkyl fragments in the gas phase upstream where the temperature is still low.

ii) the selenium compounds, which are more thermally stable, are transported to the region of the substrate and decompose in the higher temperature region where they react with the excess hydrogen to form H₂Se.

iii) the zinc and H₂Se diffuse to and adsorb on the substrate surface,

iv) hydrogen desorption to form ZnSe.

Calculation of the equilibrium constant indicates the formation of H₂Se from selenium vapor in excess hydrogen is likely. (49) However, the experimental results do not conclusively show that the selenium alkyl must dissociate in the gas phase. A mechanism similar to that for GaAs growth in which the selenium alkyl is adsorbed on the surface and reacts to form ZnSe is also plausible. For
either mechanism, the MOCVD growth process is driven by the thermal energy in the vicinity of the heated substrate.

As stated in section 2.3, the need for high temperatures in the MOCVD process can be avoided when ultraviolet light is used to photodissociate the metalorganic compounds. Excitation of gas-phase species or surface-adsorbed species is possible by either irradiating the gas above the surface or directly irradiating the surface, which must also irradiate the gas above the surface as well. The deposition process is then driven by the gas-phase photolysis of the metalorganic compounds and not by thermally driven decomposition or reaction. (15) The photo-assisted growth mechanism is thought to include six steps:

i) gas-phase photolysis of reactants
ii) diffusion of photolysis products to surface
iii) adsorption of photolysis products onto the surface
iv) surface processes such as surface diffusion and lattice incorporation
v) desorption of by-products
vi) diffusion of by-products through boundary layer into the gas stream

ArF excimer laser radiation should theoretically dissociate metal alkyls into the metal atom and alkyl radicals through a single photon process. (45) This results in a supersaturation of the II-VI elements or compounds in the vapor phase. The photolysis products then diffuse to the surface where they are adsorbed and incorporated into the crystal lattice. Since the atoms must move on the surface to appropriate lattice sites, it is likely that there is a minimum temperature at which good quality crystal growth can occur. But, since
ultraviolet energy is used to overcome the activation energy required for
dissociation of the reactants, film growth can occur at much lower temperatures
than in conventional MOCVD.

2.5 Substrate Material Considerations

The nature of the substrate is an important consideration in the epitaxial
growth of single crystal films. The term epitaxy is derived from the Greek words
epi, "upon," and taxis, "ordered." In epitaxy, a material is deposited upon a
crystalline substrate, and the deposited material takes on the crystal structure
and the orientation of the substrate. Consequently the crystal symmetry of the
substrate must match that of the film which will be grown. Likewise, both the
lattice parameter and the coefficient of thermal expansion must be similar for the
two materials. Choice of a homo-epitaxial system, in which the same material is
used for both the substrate as well as the overlayer, ensures that these
properties will be the same. In the case of ZnSe, however, large, high quality
bulk-grown crystals are difficult to obtain. Therefore, other crystalline materials
must be used as substrates for ZnSe epitaxy.

In order to obtain high quality material, a close match between the lattice
spacing of the substrate and the epitaxial layer is required. Both GaAs and Ge
have lattice parameters which are close to that of bulk ZnSe, and are therefore
good candidates for use as substrates in the hetero-epitaxial growth of ZnSe.
The lattice mismatch is only 0.32% between ZnSe and GaAs and only 0.20% in
the ZnSe-Ge hetero-epitaxial system. An exact lattice match can be attained by
the substitutional addition of a small amount of sulfur to the ZnSe film during
growth, with ZnS\textsubscript{x}Se\textsubscript{1-x} (X = 0.06) being lattice-matched to GaAs at room temperature. (50)

The majority of ZnSe epitaxy researchers in recent years have used (100) GaAs substrates with the (100) substrate misoriented 2° towards <110> to facilitate nucleation and growth. The small lattice mismatch between GaAs and ZnSe causes some distortion of the epilayer at the ZnSe/GaAs interface, resulting in stacking faults and dislocations. These defects influence the electrical and luminescent properties of the film.

The variation in lattice parameter of MOCVD grown ZnSe epilayers on (100) GaAs was measured by Mitsuhashi et al. as a function of layer thickness to study film strain caused by the small lattice mismatch between the two materials. (51) Accurate measurements of the lattice constant for the ZnSe overlayers were made using X-ray rocking curves and were compared to the value for bulk ZnSe. They found that at film thicknesses greater than a critical value, 0.15 μm, misfit dislocations began to form to relax film strain. A transition between strained and relaxed lattices appeared to occur gradually with increasing thickness up to approximately 1 μm where the lattice constant matched that for bulk ZnSe. Layers thinner than 0.15 μm were defect free but exhibited compressive strain from the lattice mismatch. To accommodate the lattice mismatch, the ZnSe lattice becomes compressed in the growth plane and elongated in the direction perpendicular to the surface. For this reason, the measured lattice parameter of films under compressive strain is larger than the bulk value. The lattice constant decreased monotonically with film thickness up to approximately 1 μm where the lattice constant for bulk ZnSe was reached.
This change in lattice constant was a result of relaxation by the formation of dislocations to alleviate the compressive strain.

The effect of lattice mismatch on the ZnSe/GaAs system was also examined by Fujita et al. (4) The crystallographic, electrical, and photoluminescent properties of heteroepitaxial ZnSe layers grown by low pressure MOCVD were studied as a function of film thickness. The lattice distortion was found to relax at a distance of one to two microns from the interface, a finding in agreement with the study by Mitsuhashi et al. (51) Both electrical and photoluminescence properties were strongly dependent on film thickness. Thin layers (<0.5 μm) exhibited high resistivity while thicker undoped films showed n-type conductivity. The Hall mobility at 77 K increased with thickness while the carrier compensation ratio decreased. For thinner films the lower carrier mobility was attributed to the incorporation of Na and Li impurities which were found to have accumulated near the interface. The high acceptor impurity concentration compensated the majority carriers and caused a reduction in carrier mobility. (Aluminum was observed in the films at a concentration of 10^{17} cm^{-3}. The researchers hypothesized that the donor was a contaminant in the dimethylzinc (DMZ) source.) Fujita et al. hypothesized that the impurities were more easily incorporated into the film near the interface where the dislocation density was highest. Lattice mismatch may have also facilitated gallium out-diffusion from the GaAs substrate into the strained ZnSe layer.

Variations in the photoluminescence (PL) spectra were observed for films of different thicknesses. (The reader is referred to section 3.3 for information about PL analysis of defects in ZnSe.) The PL spectrum at 300 K from thicker
ZnSe epilayers contained strong donor-bound-exciton emission at 2.689 eV and very weak self-activated emission centered near 2.08 eV. A 0.5 μm thick layer exhibited weaker intensity emission from the donor-bound exciton and stronger self-activated emission relative to the excitonic peak. Several deep-level emission bands were also observed at longer wavelengths, which could be due to dislocation or impurity related deep centers. The line width of the excitonic emission was found to increase with decreasing film thickness. Dean (52) observed similar trends in the PL spectrum of MOCVD grown ZnSe as a function of thickness. Luminescence efficiency was observed to decrease as film thickness decreased to less than 0.5 μm while bound-exciton and free-exciton emissions broadened. Donor-acceptor recombination bands due to Na contamination were also found for films with layer thickness of approximately 0.5 μm. The observed trends in the electrical and photoluminescence properties could result from the accumulation of impurities and dislocations in a region near the interface.

Several researchers tried to overcome the problems associated with the ZnSe/GaAs lattice mismatch by growing the alloy ZnS\textsubscript{x}Se\textsubscript{1-x} on GaAs. (50, 53, 54, 55) Matsumura et al. (53) determined that the alloy was lattice matched to GaAs with a composition ZnS\textsubscript{x}Se\textsubscript{1-x} (x = 0.04 to 0.08). The ratio of the free exciton to donor-bound-exciton emissions in the PL spectrum was highest under the lattice-matched condition indicating that the incorporation of impurities was decreased in the strain-free deposit. However, there was also an increase in the intensity of the shallow donor-acceptor-pair recombination and neutral acceptor-bound-exciton emissions with increasing sulfur content. An increase in the resistivity of the films and a decrease in carrier mobility was
also observed near the lattice matching composition. Ionized impurity scattering was also found to increase with increasing sulfur content. Therefore the higher resistivity was more likely due to increase in shallow acceptors (which was verified by PL) than from the growth of a more intrinsic material. The researchers attributed this behavior to impurities in the ZnS source. Other researchers determined that less gallium out-diffusion occurs with lattice-matched ZnS$_x$Se$_{1-x}$ (x$\sim$0.06).

The impact of lattice mismatch on epitaxial film quality has been demonstrated by the findings of the researchers mentioned above. In fact, the difference in the thermal expansion coefficient between ZnSe and GaAs makes the lattice mismatch even greater at the growth temperatures used in both MBE and MOCVD techniques. Defects are introduced to achieve strain free films under the growth conditions. But, the difference in thermal expansion introduces thermoelastic strain (tensile) in the layer as the film cools to room temperature. (3, 56)

Choice of substrate orientation as well as lattice constant is critical to achieving good quality epitaxy. Stutius and Werthen (57) carefully investigated the effects of the orientation of both GaAs and Ge substrates on the properties of ZnSe films grown by thermal MOCVD. Although there was no significant dependence of carrier concentration on substrate orientation, carrier mobility was strongly influenced by this parameter. The mobility was highest for films grown on (100) GaAs, while it significantly decreased for films grown on (110)-oriented substrates and went almost to zero for films grown on (111) substrates. The decrease in mobility was correlated with defects in the films seen with high-resolution transmission electron microscopy. In films grown on either
(110)- or (111)-oriented substrates, extended stacking faults and twinning (grain boundaries) were evident. It is highly likely that electron scattering from these defects resulted in the poor mobility which was observed on (110)- and (111)-grown films. In films grown on (100) substrates, few of these extended defects were observed. Rather, isolated interstitial Frank loops, which involve an extra (111) plane, with diameters from 30 Å to 120 Å were present. These defects are associated with extrinsic stacking faults. They have electronic levels within the band gap of ZnSe and can act as compensating impurities.

Stutius and Werthen also examined the PL spectra of films grown on different substrate orientations. They found a much higher ratio of bound-exciton emissions to lower energy emissions from films grown on (100) substrates as compared with those grown on (110) and (111) oriented substrates.\textsuperscript{(57)} The deep level emissions completely dominated the photoluminescence spectra from films on (111) substrates.

Stutius and Ponce \textsuperscript{(58)} have correlated observed defect structures to different growth processes on substrates of various orientation. The (111)B plane is the natural growth plane in the zincblende structure. For growth on the (100) substrate, there is a large angle (54° 44') between the (111) planes and the growth surface. There are, therefore, many nucleation sites on the surface and few extended defects occur. On the other hand, for growth on (110) and (111) GaAs, the angle between the (111) plane and the growth surface are relatively small. Stutius and Ponce hypothesize that the growth process on these surfaces starts with the nucleation of steps in the (111)B plane that subsequently grow laterally, resulting in step overgrowth and the formation of twinning and stacking faults. \textsuperscript{(58)}
The ideal substrate for epitaxy would of course be one of the same material that is grown because the crystallographic and thermal properties are identical. However, good quality bulk ZnSe crystals are difficult to manufacture. GaAs is very closely matched in lattice spacing and thermal expansion to ZnSe, and has been widely used as the substrate for ZnSe heteroepitaxy. The (100) GaAs orientation has resulted in films exhibiting the best quality. Therefore, (100) GaAs substrates, misoriented 2° off orientation, were chosen as the substrate material for this study.
Chapter 3

Properties of Zinc Selenide

Some important properties of zinc selenide are summarized for reference in this chapter. Data are presented on the crystallographic, thermal, electrical, optical, and thermodynamic properties of this material and on GaAs for comparison. For a more complete review, the reader may consult references (59) and (60).

3.1. Crystallographic Properties

Zinc selenide can crystallize in the wurtzite or zincblende structures at normal pressures. The wurtzite structure is a hexagonal close packed sublattice with one-half the tetrahedral interstices occupied by the opposite atom. However, this structure is metastable and is usually observed only during the onset of growth. (61) Two lattice constants are required to characterize the dimensions of the hexagonal wurtzite unit cell; $a_{\text{hex}}$ and $c_{\text{hex}}$, the width and height of the unit cell. These are 4.01 Å and 6.54 Å respectively for ZnSe. (61) The stable crystal structure of ZnSe (and GaAs) is the sphalerite form, otherwise known as the zincblende structure. This structure is very similar to that of diamond and silicon, except each atom in the crystal lattice is tetrahedrally surrounded by four atoms of the other element. The lattice can be visualized as two interpenetrating face centered cubic (fcc) lattices, with the zinc sublattice shifted into tetrahedral interstices of the Se sub-lattice. One unit cell contains four ZnSe units, consisting of an fcc Zn (or Se) cell with Se (or Zn) atoms in one half of the tetrahedral interstices (Fig. 3.1.1). The ZnSe lattice
constant, $a_0$, is reported as 5.669 Å. The lattice constant for both the zincblende and wurtzite are listed in Table 3.1.1 along with nearest neighbor spacings in the zincblende crystal.

Figure 3.1.1 Zincblende structure of zinc selenide.

The stacking sequences for zincblende structure of ZnSe is shown in Figure 3.1.2. The zincblende structure is repeated after three Zn and three Se layers. One important feature of the zincblende structure is the lack of inversion symmetry along $<111>$ directions. Notice that the ZnSe$_4$ tetrahedra are oriented along the $<111>$ direction. As a consequence of this nonsymmetry,
Table 3.1.1. Crystallographic Properties of ZnSe and GaAs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Lattice Constant (Å)</th>
<th>d(M-X) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Zincblende</td>
<td>$a_0 = 5.669$</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>Wurtzite</td>
<td>$a_{hex} = 4.01$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$c_{hex} = 6.54$</td>
<td></td>
</tr>
<tr>
<td>GaAs&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Zincblende</td>
<td>$a_0 = 5.653$</td>
<td>2.44793</td>
</tr>
</tbody>
</table>

<sup>a</sup> - reference 61

<sup>b</sup> - reference 63

zincblende crystals are polar and exhibit piezoelectricity. The polar (111) surfaces in ZnSe zincblende crystals terminate either with Zn or with Se atoms. These surfaces are labeled A if they terminate with Zn and B if they were covered with Se atoms. (see Fig. 3.1.2) This difference in the surface species of (111) A and (111) B planes results in asymmetries in crystal growth and chemical reactivity. For instance, chemical etching of (111)A ZnSe surfaces with $K_2Cr_2O_7 - H_2SO_4$ typically results in a polished surface, whereas etched (111)B ZnSe surfaces exhibit triangular pyramidal pits. (61) The growth rate along the <111>B directions in ZnSe is faster than that along <111>A. Therefore, the growth planes in ZnSe are of the (111)B type. (58) Due to the anisotropy of the growth rates in the <111> directions, the morphology of ZnSe
thin films is strongly dependent on the orientation of the substrate. (see section 2.4)

Figure 3.1.2. Stacking sequences for zincblende structure.

(From H. Hartmann et al. (61))
3.2. Thermal Properties

Material properties and some important thermal properties for ZnSe and GaAs in the zincblende structure at 300 K are presented in Table 3.2.1.

Table 3.2.1. Physical and Thermal Properties of ZnSe and GaAs

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>ZnSe(^a)</th>
<th>GaAs(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>(g·mol(^{-1}))</td>
<td>144.3</td>
<td>144.7</td>
</tr>
<tr>
<td>Density</td>
<td>(g·cm(^{-3}))</td>
<td>5.42</td>
<td>5.317</td>
</tr>
<tr>
<td>Melting Point</td>
<td>K</td>
<td>1790</td>
<td>1511</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>W cm(^{-1}) K(^{-1})</td>
<td>0.19</td>
<td>0.55</td>
</tr>
<tr>
<td>Thermal Expansion Linear Coeff. @25 °C</td>
<td>10(^{-6}) °C(^{-1})</td>
<td>6.8</td>
<td>5.73</td>
</tr>
<tr>
<td>Phonon Frequency</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LO (F)</td>
<td>(meV)</td>
<td>31.3</td>
<td>36.13</td>
</tr>
<tr>
<td>TO (F)</td>
<td>(meV)</td>
<td>26.4</td>
<td>33.25</td>
</tr>
</tbody>
</table>

\(^a\) - reference 64

\(^b\) - reference 63
3.3. Optical Properties - Photoluminescence

The photoluminescence properties of ZnSe are useful for thin film analysis. ZnSe, with a direct band gap of 2.67 eV at room temperature, has a high luminescence efficiency. When a ZnSe film is illuminated with a light source of energy greater than the band gap, electrons are excited into the conduction band forming excess electron-hole pairs in the sample. These carriers are subsequently trapped, form excitons or otherwise relax to lower energies. They may then radiatively recombine and emit light characteristic of the energy levels they were occupying. Impurities and defect centers can be identified from the transition energies detected in the luminescence from the radiative recombination processes. Transitions associated with band-to-band recombination, donor or acceptor bound species recombination, associated donor-acceptor pair recombination and deep acceptor centers may occur (see Fig. 3.3.1).

Excitonic emissions dominate the low temperature photoluminescence spectrum of ZnSe. Excitons are electron-hole pairs that relax into a hydrogen-like configuration as a result of Coulomb attraction. The electron and hole of the exciton have greater interaction than free carriers because their wave functions are localized to one another and, therefore, the probability for recombination of excitons is much greater than that for free carriers. The binding energy of the lowest energy free exciton is theoretically 25.7 meV and an exciton's average lifetime is on the order of $10^{-9}$ s at 4 K. (65) Since an exciton contains both types of carriers, it does not contribute to electrical conduction. The strong
electron-phonon interaction in this material results in phonon coupling to the exciton levels for high quality ZnSe. Therefore, free exciton emission is found at

$$E_{FE} = E_g - E_B - n\hbar\omega_{LO} \ n = 0, 1, 2, 3, .. \quad (3.3.1)$$

where $E_g$ is the band gap, $E_B$ the free exciton binding energy, and $\omega_{LO}$ is the longitudinal optical (LO) phonon frequency which is approximately 31.9 meV.

![Diagram](image)

Figure 3.3.1 Recombination processes (a) band-to-band, (b) bound exciton, (c) free electron to bound hole, (d) donor-acceptor, (e) free electron-deep acceptor, and (f) exciton at isoelectronic center.
in ZnSe. (66) The band gap $E_g$ of ZnSe, which increases with decreasing temperature, is 2.83 eV at 4 K. (67) The free exciton emission is often observed near 2.803 eV. Strain in the film causes a splitting of degenerate energy levels in the valence band, resulting in a decrease in the band gap. This is observed as a shift in the observed position of excitonic emissions to lower transition energies by several meV. (52)

Excitons bind readily to neutral and ionized donors or acceptors, donor-acceptor pairs and deep centers. Emissions from bound excitons are labeled $I_2$ lines for neutral donors and $I_1$ lines for neutral acceptors. Bound exciton emission may also exhibit LO phonon coupling in high quality films, with typically stronger coupling observed to bound excitons than to free excitons. The transition energy for bound excitons, $E_{BE}$, is

$$E_{BE} = E_g - E_x - E_{BX} - n \hbar \omega_{LO} \quad n = 0, 1, 2, 3, \ldots$$

(3.3.2)

where $E_x$ is the impurity ionization energy and $E_{BX}$ is the bound exciton binding energy. The small binding energies of free and bound excitons make low temperature analysis necessary for study of these transitions. At temperatures $kT > E_{BX}$ or $E_B$, the excitons will dissociate before they can radiatively recombine. The temperature for the onset of observation of the neutral donor-bound-excitons in ZnSe is about 46 K. At higher temperatures, free carrier transitions dominate. The energy levels of bound excitons in ZnSe observed by photoluminescence at 4.2 K are given in Table 3.3.1. (68) $I_1$ emission lines signify the recombination of excitons bound to neutral acceptors, $I_2$ lines represent the recombination of excitons bound to neutral donors and $I_3$ lines are
those associated with recombination to ionized donors. The width of the bound-exciton transitions is broader for polycrystalline films than for single crystal films. For MOCVD grown films, the spectral width of the donor-bound-exciton emission is \( \sim 1 \text{ meV} \) for single crystal films, but it can increase by several meV due to defects introduced as a result of strain in the film. Polycrystalline MOCVD ZnSe films, on the other hand, have spectral widths of about 10 meV for these transitions. (52)

Several types of donor-acceptor pair recombination bands have been observed in ZnSe. The introduction of the shallow acceptors Li and Na into ZnSe results in donor-acceptor pair spectral bands at 2.69 eV (\( Q_0 \)) and 2.68 eV (\( P_0 \)), respectively, with strong LO phonon replicas. (69) Another band (\( R \)) with broader transitions at slightly higher energy (2.71 eV) has been observed. The species responsible for the \( R \) band are unknown, but it is thought that the donor and acceptor have comparable ionization energies. (66) The photon energy

Table 3.3.1. Energy levels of bound excitons in ZnSe (4.2 K) (68)

<table>
<thead>
<tr>
<th>Component</th>
<th>Transition Energy (eV)</th>
<th>Component</th>
<th>Transition Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_1^{\text{DEEP}} )</td>
<td>2.7829, 2.7831</td>
<td>( I_2^F )</td>
<td>2.7970</td>
</tr>
<tr>
<td>( I_1^i )</td>
<td>2.7921</td>
<td>( I_2^n )</td>
<td>2.7972</td>
</tr>
<tr>
<td>( I_1^{\text{Na}} )</td>
<td>2.7930</td>
<td>( I_2^{\text{Ga}} )</td>
<td>2.7975</td>
</tr>
<tr>
<td>( I_3^n )</td>
<td>2.7941, 2.7945</td>
<td>( I_2^{\text{Cl}} )</td>
<td>2.7977</td>
</tr>
<tr>
<td>( I_3^{\text{Cl}} )</td>
<td>2.7959, 2.7963, 2.7965</td>
<td>( I_2^{\text{Al}} )</td>
<td>2.7977</td>
</tr>
</tbody>
</table>
emitted from the donor-acceptor pair recombination at low temperatures is dependent on excitation energy, delay time after excitation and film strain. The band maxima shift to higher energies with increasing excitation energy and to lower energies with time delay. Strain in the film also causes a shift to lower transition energies. (52)

Two other deep bands that occur in the PL spectra of MOCVD grown films have been associated with dislocations in the film. Deep bands Y and S are common for MOCVD grown ZnSe films and are enhanced when substrate preparation or reactor leak-tightness is poor. (52) The Y band at 2.60 eV is a sharp peak that exhibits weak LO phonon coupling. The S band at about 2.5 eV is a broad transition, within which weak LO phonon coupling can also be resolved. The intensity of the Y and S bands was observed to increase with growth temperature to a maximum at 450 °C and above. It has been hypothesized that the Y and S bands are associated with dislocations and dislocation-associated impurities. (70) Gallium is one likely impurity that could be associated with these emissions since the amount of Ga out-diffusion from the substrate would increase with increasing temperature.

Deep acceptor complexes and isoelectronic impurity centers are evident in photoluminescence spectra of ZnSe as very broad transitions at energies below 2.4 eV. The "self-activated" center in ZnSe is a deep acceptor with broad emission centered near 2.1 eV. (52) The doubly ionized zinc vacancy-donor (V_{Zn}^{n=2} - D^+) complex acts as an acceptor and is known to be involved in the self-activated luminescence band. (71) A shift to higher energy was observed for the broad band emission from MOCVD grown ZnSe when film thickness was
decreased, changing from 2.1 eV at 2.2 μm film thickness to approximately
2.35 eV at 0.14 μm film thickness. (52)

Figure 3.3.2 contains three examples of photoluminescence spectra of
ZnSe heteroepitaxial films at 4.2 K. The sharp transitions near 2.8 eV are from
bound-exciton recombination. Emission from donor-bound exciton
recombination is observed at slightly higher energies than acceptor-bound
exciton recombination (see Table 3.3.1). Weak donor-acceptor recombination
emission is observed in the top spectrum, with no-phonon line near 2.7 eV and
two phonon lines at lower energies spaced at 32 meV intervals. The presence
of multiple phonon lines is an indication of an extended crystal lattice.

Features in the region below 2.6 eV in the photoluminescence spectra
are related to defects in the epitaxial films. The top spectrum contains the Y and
S bands at 2.6 eV and 2.5 eV respectively, which arise from the presence of
dislocations and dislocation associated impurities. The broad emission present
in all three spectra is a result of the self-activated center. Since the self-
activated center is, in part, due to the presence of native defects such as
vacancies, the presence of this emission can be used as an indication of film
quality. A high ratio between the donor-bound exciton (DBE) emission relative
to self-activated peak (SA) intensity indicates a low concentration of native
defects and a high quality film. Using this criteria, the film that exhibited the
middle photoluminescence spectrum in Figure 3.3.2 should have the highest
quality, while spectrum (c) with no excitonic emission is indicative of a very poor
quality film with little or no extended crystal lattice.
Figure 3.3.2. Examples of photoluminescence spectra of ZnSe heteroepitaxial films at 4.2 K.
3.4. **Electrical Properties**

The electrical properties that characterize a semiconductor material are its conductivity, $\sigma$, the free carrier concentrations and type (n or p), and carrier mobilities $\mu_n$ and $\mu_p$. These properties can be measured experimentally using the van der Pauw Hall method, which is discussed in Section 5.8.

Impurities and native defects have the strongest influence over electrical properties in II-VI compounds. They act as a source of extrinsic carriers which dominate the contributions to carrier concentration. They also act as scattering centers which limit carrier mobility. Due to its large band gap, the intrinsic carrier concentration in ZnSe is negligible compared to extrinsic carrier concentrations. At a room temperature band gap of 2.67 eV and effective electron and hole masses of 0.17 $m_o$ and 0.6 $m_o$ respectively ($m_o = \text{free electron mass}$), the intrinsic carrier concentration, $n_i$, is only on the order of $10^{-4}$ cm$^{-3}$ in ZnSe. (72) This is negligible compared to typical impurity and native defect concentrations which can be as high as $10^{17}$ cm$^{-3}$ in "high purity" n-type material. (35, 72) Thus, the room temperature carrier concentration of n-type ZnSe can be approximated as $n = N_D - N_A$, where $N_D$ and $N_A$ are donor and acceptor concentrations, respectively. Substitutional donor and acceptor species in ZnSe are listed in Table 3.4.1 with their ionization energy, $E_D$ and $E_A$.

Controlled doping of II-VI compounds is difficult due to carrier compensation effects. The introduction of donor or acceptor species may result in the formation of intrinsic defects of the opposite conductivity type. For example, it is thought that the introduction of extrinsic donors leads to the
formation of doubly charged zinc vacancies which act as acceptors, reducing the effective carrier concentration.

There is some debate over what type of defect complex is responsible for compensation. (73, 74) The term *self-compensation* arises from the assumption that the compensating defects are intrinsic in nature, such as vacancies or native interstitials. However, compensation can also occur with amphoteric

| Table 3.4.1 Donor and acceptor species in ZnSe. (75) |
|---------------------------------|-----------------|
| Species                        | Ionization energy (meV) |
| Donors                         |                 |
| Al                             | 26.3            |
| Cl                             | 26.9            |
| Ga                             | 27.9            |
| In                             | 28.9            |
| F                              | 29.3            |
| Acceptors                      |                 |
| Li                             | 114             |
| Na                             | 90-128          |
| N \(^1\)                       | 80-112          |

1 = reference 76

dopants or impurities. For example, Li acts as an acceptor on a Zn site, but if a Li atom occupies an interstitial, it is a donor. It has been difficult to obtain high
conductivity material in ZnSe due to the high concentration of compensating defects introduced into the material, especially in thin films which would be required for device applications. Whether the difficulty with controlled doping in ZnSe is caused by self-compensation or the lack of good dopant candidates (especially for p-type material) is not known.

Carrier mobility is limited by scattering with phonons, impurities and other carriers. Ruda (72) carried out a theoretical analysis of electron transport in lightly doped n-type ZnSe. The contributions due to scattering from acoustic and optical phonons, piezo-electric phonons, and impurities to the reduction in electron mobility were calculated. The values for the material parameters used in his calculations are shown in Table 3.4.2. At room temperature and carrier concentrations below approximately $10^{18}$ cm$^{-3}$ the dominant carrier scattering occurs by interactions with polar optical phonons, partly a result of the high ionicity of ZnSe. Impurity scattering is the limiting process at higher doping levels and lower temperatures (77 K). A maximum electron mobility of approximately $10^4$ cm$^2$/Vs and 800 cm$^2$/Vs is expected at 77 K and 300 K respectively, with electron concentrations on the order of $10^{15}$ cm$^{-3}$ in uncompensated material. Compensation will result in a reduction of the electron mobility because the total ionized impurity concentration is increased for a given electron concentration. There has not been a similar theoretical analysis on hole transport in p-type ZnSe, but experimental values for p-type mobility have been on the order of 100 cm$^2$/Vs. (8,26)
Table 3.4.2. Material parameters used for mobility calculations by Ruda

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hole effective mass</td>
<td>0.60</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.17</td>
</tr>
<tr>
<td>Energy gap (300 K) (eV)</td>
<td>2.70</td>
</tr>
<tr>
<td>High-frequency dielectric constant</td>
<td>6.20</td>
</tr>
<tr>
<td>Low-frequency dielectric constant</td>
<td>9.20</td>
</tr>
<tr>
<td>Optical phonon energy (meV)</td>
<td>31.40</td>
</tr>
<tr>
<td>Polar phonon Debye temperature (K)</td>
<td>364</td>
</tr>
<tr>
<td>Optical mode coupling constant</td>
<td>0.47</td>
</tr>
<tr>
<td>Longitudinal elastic constant (10^{10} Nm^{-2})</td>
<td>10.34</td>
</tr>
<tr>
<td>Intervalley deformation potential constant (eV)</td>
<td>4.20</td>
</tr>
<tr>
<td>Piezoelectric coefficient</td>
<td>0.02283</td>
</tr>
</tbody>
</table>

3.5 Thermodynamic Properties

Thermodynamics defines the driving force in the epitaxial growth process. For the simplified process of gaseous zinc and selenium condensing to form a solid

\[ \text{Zn(g)} + \frac{1}{2} \text{Se}_2(g) \rightarrow \text{ZnSe(s)} \]  

(3.5.1)

film growth will occur when

\[ p(\text{Zn}) p_{\text{Se}_2}^{\frac{1}{2}} \gg \frac{a_{\text{ZnSe}}}{K_p} \]  

(3.5.2)
\( K_p \) is the equilibrium constant, \( p_i \) the Zn and Se\(_2\) partial pressures and \( a_{\text{ZnSe}} \) the activity of the solid ZnSe. The calculated temperature dependence of the equilibrium constant for this reaction is (59)

\[
\log(K_p^{-1}) = 29.21 - 38377 \, T^{-1} - 3717 \, T^{-2} - 2.67 \log T - 2.67 \times 10^{-4} T \tag{3.5.3}
\]

where \( T \) is in degrees Kelvin. The value of \( \log(1/K_p) \) ranges from \(-1.1 \times 10^7\) at 400 K to \(-2.4 \times 10^7\) at 900 K, meaning that \( K_p \) is very large and the quotient on the right-hand side of equation 3.5.2 is nearly zero. Typical partial pressures for the Zn and Se sources used during this study were 0.125 torr and 1.25 torr respectively. Assuming that all the metalorganic molecules break down completely, the system was easily supersaturated with the sources to drive film growth.

Thermodynamic data for ZnSe and compounds relevant to film growth are given in Table 3.5.1. The standard heat of reaction for dimethylzinc and diethylselenide reacting to form ZnSe, methane and ethane is \(-51.15\) kcal/mol.

The material presented in this chapter is included for reference on the important physical, optical, electrical and thermodynamic properties of ZnSe. The large direct band gap of 2.67 eV makes ZnSe a good candidate for blue optoelectronic devices, but controlled doping to fabricate p-n junctions is difficult in part because of the formation of electrically compensating defects. However, the native defect density (e.g. vacancies) is reduced with film growth at lower temperatures indicating material grown under the lower temperature conditions of photo-assisted epitaxy may have fewer defects.
Table 3.5.1  Thermodynamic properties of ZnSe and related elements and compounds.

<table>
<thead>
<tr>
<th>Component</th>
<th>$\Delta H^\circ_{298}$ (kcal/mol)</th>
<th>$\Delta G^\circ_{298}$ (kcal/mol)</th>
<th>$S^\circ_{298}$ (cal/K mol)</th>
<th>$\Delta H^\circ_V$ (kcal/mol)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe(s)</td>
<td>-39.3</td>
<td>-39.3</td>
<td>19.8</td>
<td>175.0</td>
<td>(77)</td>
</tr>
<tr>
<td>Zn(s)</td>
<td>0</td>
<td></td>
<td>9.95</td>
<td></td>
<td>(77)</td>
</tr>
<tr>
<td>Zn(g)</td>
<td>31.19</td>
<td></td>
<td>38.45</td>
<td></td>
<td>(77)</td>
</tr>
<tr>
<td>Se(g)</td>
<td>48.37</td>
<td></td>
<td>42.21</td>
<td></td>
<td>(77)</td>
</tr>
<tr>
<td>Se$_2$(g)</td>
<td>33.14</td>
<td></td>
<td>60.2</td>
<td></td>
<td>(77)</td>
</tr>
<tr>
<td>(CH$_3$)$_2$Zn</td>
<td>5.04 (l)</td>
<td></td>
<td></td>
<td>7.05</td>
<td>(78)</td>
</tr>
<tr>
<td></td>
<td>12.09 (g)</td>
<td></td>
<td></td>
<td></td>
<td>(78)</td>
</tr>
<tr>
<td>(C$_2$H$_5$)$_2$Se</td>
<td>-23.04(l)</td>
<td></td>
<td></td>
<td>9.30</td>
<td>(78)</td>
</tr>
<tr>
<td></td>
<td>-13.74 (g)</td>
<td></td>
<td></td>
<td></td>
<td>(78)</td>
</tr>
</tbody>
</table>

$\Delta H^\circ_{298}$ = standard enthalpy of formation at 298 K

$\Delta G^\circ_{298}$ = standard free energy of formation at 298 K

$S^\circ_{298}$ = standard entropy at 298 K

$\Delta H^\circ_V$ = standard heat of vaporization
Chapter 4
Experimental Apparatus

4.1 System Overview

Figure 4.1.1 is a schematic of the experimental apparatus designed for the laser-assisted MOCVD growth of compound semiconductors. Thus far, the system has been used solely for the growth of zinc selenide epitaxial films. The major sub-systems included i) the hydrogen carrier gas purification, ii) the metalorganic bubbler transport systems, iii) the reactor, iv) the exhaust system with a pyrolysis furnace, particle filters, and vacuum pump, v) the system control electronics with safety interlocks and vi) the excimer laser with necessary optics. A detailed description of these sub-systems follows in Sections 4.2 through 4.6.

The gas manifold, reactor and exhaust line were all constructed using stainless steel tubing. Most of the tube connections were welded or were sealed using VCR fittings with silver-plated nickel gaskets. The manifold and exhaust line tubing were purchased with an electropolished finish on the interior wall to eliminate particulate contaminants, but were also etched after welding was completed. A dilute solution of HNO₃ and HF acids was pumped through each section of tubing to remove any scale formed during welding and to passivate the surface. All tubing and fittings were carefully examined for leaks using a helium leak detector after the system was assembled.

The entire reactor system was built inside a Plexiglass safety enclosure with 1/4" walls. The three feet wide by eight feet long and eight feet high enclosure was constructed around a Uni-Strut frame structure. Two exhaust fans kept sufficient air flow to maintain a slight negative pressure between the
enclosure and the laboratory. Dangerous fumes released from the reactor system were diluted and exhausted to the outside.

![Diagram of experimental MOCVD growth apparatus](image)

**Figure 4.1.1** Schematic of the experimental MOCVD growth apparatus.

A. hydrogen carrier purification system, B. metalorganic bubbler transport system, C. reactor and D. exhaust system.

All electronics for flow rate control, pressure control, substrate heating and valve sequencing were rack-mounted in a cabinet to the side of the enclosure. Nine mass flow controllers (MFCs) regulated the flow rates of the hydrogen gas streams and three pressure control systems maintained constant pressure in the two metalorganic bubblers and in the reactor. Gas cylinders
used for the LMOCVD system and the excimer laser were located in a gas cabinet equipped with an exhaust fan.

4.2 Hydrogen Carrier Gas Purification

Ultrapure hydrogen carrier gas was obtained by diffusing hydrogen through a palladium alloy barrier in a commercial purification unit (Johnson-Matthey Inc. HP-50-VCR). The palladium alloy barrier can be damaged by the heat evolved during reactions of hydrogen with some gases such as oxygen. The transport rate through the barrier will decrease with excessive contamination and particulate build-up. Therefore, the hydrogen was treated before admission to the palladium diffusion system in order to lengthen the lifetime of the purifier. Extra-dry grade cylinder hydrogen was first passed through a particle filter to remove all particles down to 0.1 μm in size with 99.9999% efficiency. Then oxygen was removed with a Johnson-Matthey OR-50 purifier, which catalytically reacted any oxygen present with hydrogen to form water. The water was removed with a sodium aluminosilicate 4A molecular sieve before the gas entered the palladium alloy purifier.

The hydrogen purification unit was rated for 50 standard liters per minute (slm) hydrogen when the cell was heated to 400 °C to 425 °C with an inlet pressure of 200 psig and the outlet at atmospheric pressure. The mass flow controllers for regulation of the gas flow required a 30 psi drop between their inlet and outlet for proper operation. At the transport rate of 2.5 slm that was used for the majority of the MOCVD growth experiments, a purifier inlet pressure of 40 psig was sufficient to obtain the necessary outlet pressure for reliable control of the gas flow rates.
Proper shutdown and power-up procedures were required to prevent damage to the Pd alloy barrier. If the purifier were heated up or cooled down with hydrogen present, grain growth could occur in the alloy that would severely limit the hydrogen transport rate. An extra supply line of ultrahigh purity helium, also filtered for particles, and a vacuum line were connected upstream of the purifier to pump out and back-fill the purifier prior to shutdown. The reactor was purged with helium from this source after the chamber was opened to atmosphere.

4.3 Metalorganic Source Materials and Bubbler Transport Systems

Dimethylzinc and diethylselenide were the metalorganic sources used in these experiments. These materials are high vapor pressure liquids like most other metalorganic compounds in MOCVD. The temperature dependence of the vapor pressures of dimethylzinc (DMZ) and diethylselenide (DESe) could be approximated by the equations from the supplier, Alfa Products.

$$\log \left( P_{DMZ} \right)_{(\text{torr})} = 7.802 - 1560/T(K) \quad (4.3.1)$$

$$\log \left( P_{DESe} \right)_{(\text{torr})} = 7.905 - 1924/T(K). \quad (4.3.2)$$

Both sources, purchased from commercial vendors in 100 gram units, were stored in stainless steel bubblers with shut-off valves and VCR™ connections. The dimethylzinc (Stauffer Chemical Company Specialty Products Division) had a metallic composition of 99.9999% zinc and the diethylselenide (Alfa Products, A Division of Morton Thiokol) was 99.995% pure. Lot analysis of the diethylselenide showed a 34 ppm Si impurity concentration and trace amounts of S, As, Sn, and B.
These metalorganic liquids are highly pyrophoric, meaning they spontaneously combust upon exposure to air or oxygen. Therefore, extreme caution was taken to ensure that the reactor system was leak tight and that any unreacted material was destroyed.

The dimethylzinc and diethylselenide were transported to the MOCVD reactor using a conventional bubbler transport technique. (Figure 4.3.1) Purified hydrogen carrier gas was bubbled through the liquid in the bubblers.

Figure 4.3.1. Bubbler transport system for dimethylzinc and diethylselenide.
where it is assumed that the hydrogen becomes saturated with metalorganic at its equilibrium vapor pressure and then carries the source gases to the reactor. The bubbler transport rate for the metalorganic sources was calculated using:

$$Q_{MO} = Q_{H_2} \frac{P_{MO}}{P - P_{MO}}$$  \hspace{1cm} (4.3.3)

where

- $Q_{MO}$ = metalorganic flow rate (sccm)
- $Q_{H_2}$ = hydrogen carrier gas flow rate through the bubbler (sccm)
- $P$ = total pressure in the bubbler (torr)
- $P_{MO}$ = temperature dependent vapor pressure of metalorganic source (torr)

By controlling the bubbler pressure, metalorganic vapor pressure, and carrier gas flow rate, the metalorganic source flow rate can be specified.

The hydrogen carrier gas mass flow controllers (Unit Instruments Inc. UFC-1000) were chosen to give a maximum flow rate of 20 sccm through the dimethylzinc bubbler and 200 sccm hydrogen through the diethylselenide bubbler. Immediately downstream from the bubbler, the gas stream was diluted by a factor of 5 or 10 to 1 with more carrier gas to minimize condensation on the tubing walls.

The pressure in each bubbler was measured with an absolute pressure Baratron capacitance manometer with 1000 torr range and 0.1 torr accuracy (MKS Instruments Inc. model 222CA-01000BB). Pressure control for the bubblers was achieved using automatic pressure/flow controllers (MKS model...
250B) with feedback from the pressure gauges to operate downstream throttle valves (MKS model 248A).

For control of the metalorganic vapor pressure, each bubbler was partially submerged in a (Brinkmann Instruments Lauda RMT -6) constant temperature bath containing a 1:1 water - ethylene glycol mixture. The bath temperatures could be controlled from -15 °C to 120 °C to within 0.2 °C. Under typical flow conditions, the DMZ bubbler was operated at -2.5 °C and the DESe bubbler at 55 °C to have metalorganic vapor pressures of about 110 torr in the bubbler. The tubing downstream of the DESe bubbler to the control valve was heated to ~ 50 °C to prevent DESe condensation on the walls.

4.4 LMOCVD Reactor

The LMOCVD reactor was composed of three sections: i) an inlet/mixing chamber, ii) a growth chamber and iii) an exit chamber. Figure 4.4.1 is a schematic of the reactor in cross section. The twelve inch long outer tube of 304 stainless steel had a 4-inch outer diameter and 0.083" wall. The three sections of the reactor were connected using 6-inch diameter flanges sealed with copper gaskets. The overall length of the tube was 24 inches.

The inlet section of the reactor was designed to act as a mixing chamber for the source gases before they entered the growth region. The mixing chamber consisted of the outer tube with flanges, an end flange and a conical aluminum insert. The two metalorganic sources in hydrogen and the hydrogen buffer gas were introduced through three separate 0.125" diameter holes in the endplate. The holes were located radially 1.5 inches from the center of the flow tube, all below the centerline and spaced 60° apart. A conical insert with a
Figure 4.4.1. Schematic of LMOCVD reactor in cross section.

14.6° interior angle and a 1.125" opening acted as a barrier to prevent direct streaming of the gases into the flow tube and to allow mixing of the reactants before they entered the growth region. The insert was sloped gradually on the interior to minimize turbulence in the transition region between sections where the average gas velocity decreased due to the change in tube cross section.

The growth region of the reactor consisted of the 4-inch outer diameter tube with three windows at the midsection for introduction of excimer laser radiation, and a 3.5" stainless steel tube insert to allow purging of the windows. Since the option for both perpendicular and parallel laser irradiation of the substrate was desired, the reactor was constructed such that one window port was located directly above the reactor for perpendicular irradiation experiments
and the other two ports were located on either side for those experiments in which the laser beam passed parallel to the substrate. Magnesium fluoride windows were used because of their high transmittance (~92%) at the ultraviolet ArF excimer wavelength, 193 nm. The windows (Harshaw Chemical Co.), brazed into a 2.75" knife-edge flange, had a 1.4" viewing diameter. Each window was attached to the main reactor tube at the end of a 3-inch long tube, 1.5 inches in outer diameter.

Effective purging of the windows was extremely important to prevent deposition of material on the windows. A two-stage purge scheme was designed for the reactor. First, hydrogen purge gas was introduced at each window through two-sided flanges positioned between the side tube port and the window flange. Purge gas entered through two holes opposite each other in this flange, and acted as a gaseous barrier to prevent metalorganic vapors from coming into contact with the windows. For the second stage, purge gas was introduced between the outer tube and a stainless steel insert tube and allowed to flow parallel to the main gas stream. The insert was 12-inch long with a 3.5" outer diameter and 0.035" walls. The upstream end of the insert fit snugly into the main flow tube to prevent metalorganic from entering the purge stream. Hydrogen gas was introduced through two inlets 180° apart. Four baffles parallel to the flow down the length of the tube prevented rotational flow of the purge gas. The downstream end of the insert tube was open to the inner chamber. Three 0.5" diameter holes were drilled through the insert tube to allow the laser radiation to enter the growth region. Mass flow controllers were used to accurately control the purge rates at each window and in the parallel purge stream.
The substrate was positioned on a 1 inch by 6 inch rectangular stainless steel heater that was suspended horizontally in the center of the reactor on the end of a stainless steel tube. The GaAs substrate was attached to the heater with a stainless steel clip at a position approximately three inches from the upstream edge of the heater. The growth temperature was monitored with a K-type thermocouple encased in a 0.063" stainless steel sheath, similarly clipped to the heater adjacent and downstream of the substrate. Temperature control was achieved by regulation of the power to the heater using a variable transformer. An on-off temperature controller was also connected to the heater power supply, but due to the low thermal mass of the heater the temperature fluctuations using the controller were too large. Therefore, the temperature controller was used only to turn the heater power off if the temperature inadvertently increased above an upper limit.

The exit chamber of the reactor was six inches long, consisting of the four-inch diameter outer tube and another conical aluminum insert, an end flange where all feedthroughs were located and a pressure gauge. The aluminum insert was used to prevent the formation of large circulation currents in the chamber due to reflection of gas flow off the end-plate of the reactor. The product gas exited the reactor through an 0.5" O-ring compression fitting welded through the end flange. The reactor pressure was measured and controlled using a capacitance manometer positioned vertically above the exit section of the reactor to prevent an excessive rise in temperature or an accumulation of particles in the gauge head. Pressure was controlled by using a downstream pressure control valve located near the inlet to the vacuum pump. The valve was operated by a pressure/flow controller using the output signal from the
capacitance manometer as an input. Although the feedback loop contained a large section of tubing and other equipment between the gauge and the control valve, the time constant could be adjusted to maintain a constant pressure to within several tenths of a torr under flow conditions at pressures from 100 to 760 torr.

A plexiglass model of the reactor was fabricated for flow visualization studies. Fine particles are formed when dilute gas streams containing either ammonium hydroxide and hydrochloric acid or titanium tetrachloride and water are mixed. The particles are entrained in the gas flow and thereby allow visualization of the flow patterns. Using this model we determined the ratio of purge gas flow to main tube flow that resulted in only small disturbance to the main flow at the pressures used in this study. Visualization experiments also indicated that the funnel-shaped insert at the reactor exit was necessary to prevent large reverse flow recirculation patterns. Visualization of flow during substrate heater use did show evidence of vortex formation above the heater.

All feedthroughs into the reactor were positioned on the end flange. The rod supporting the substrate heater passed through an O-ring compression fitting in the center of the flange. Gas exited the reactor through another O-ring compression fitting below the heater support rod. The reactor was connected to the exhaust system through a six-inch long flexible stainless steel hose at the O-ring compression fitting. The electrical and thermocouple feedthroughs were also located on the flange. The thermocouple feedthrough was made by drilling a 0.063" hole through a 1.33" knife-edge flange and silver-soldering the stainless steel sheath of the thermocouple directly to the flange. During the exchange of substrates, the electrical, thermocouple and gas feedthroughs
were disconnected and the entire end flange carefully removed, sliding the heater and rod through the hole in the conical insert.

Natural convection in the growth chamber can severely affect the quality of the epitaxial film. The gas heated by the susceptor will rise due to buoyancy effects while cold gas entering the reactor flows downward. A low pressure region near the roof of the reactor will be formed, and if the flow velocity is too low, reverse flow may occur resulting in the formation of recirculation eddies. Recirculation increases the probability of gas phase nucleation which can form "dust" particles of the material upstream and above the growth region. The incorporation of these dust particles into the films is detrimental to film quality.

The dimensionless quantity Grashof number divided by the Reynold's number squared (Gr/Re²) is a direct measure of the relative importance of buoyancy forces to inertial forces in the gas flow. (79) The Grashof number is defined as

\[ Gr = \frac{\rho^2 g \beta \Delta T D^3}{\mu^2} \]  

(4.4.1)

with D a characteristic dimension (tube diameter), \( \Delta T \) the temperature difference between the heat source and the wall, g the acceleration due to gravity, \( \beta \) the coefficient of volume expansion, \( \rho \) the gas density at the wall temperature and \( \mu \) the viscosity. This quantity is independent of the volumetric flow rate, and is dependent on the square of pressure through the density dependence. The Reynolds number is
\[ \text{Re} = \frac{\rho v D}{\mu} \]  

with \( v \) the average flow velocity. The square of the Reynolds number is independent of pressure and proportional to the square of the volumetric flow rate. If it is assumed that the gas mixture acts as an ideal gas, the quantity \( \frac{\text{Gr}}{\text{Re}^2} \) can be equated to a function of the controllable reactor parameters as follows: (see Appendix C)

\[ \frac{\text{Gr}}{\text{Re}^2} = \frac{\pi^2 g T_0^2}{16 P_0^2 Q_0^3} \frac{P^2 D^5 \Delta T}{T^3} \]

where \( P \) is the reactor pressure, \( T \) the gas temperature, \( Q_0 \) the flow rate under standard conditions, and \( T_0 \) and \( P_0 \) are standard temperature and pressure (25 °C, 1 atm).

Natural convection becomes important in horizontal MOCVD reactors when \( \frac{\text{Gr}}{\text{Re}^2} > 1 \). (80) This quantity is on the order of 100 under the reactor conditions used in our experiments if it is assumed that no wall heating occurs. In reality, the reactor walls would be heated during the pre-growth procedure, and since the outer wall is insulated, all heat would be dissipated into the gas, making \( \frac{\text{Gr}}{\text{Re}^2} \) lower. However, the wall heating was probably insufficient to prevent severe natural convection problems in the current reactor.

A new reactor was designed to eliminate natural convection in the MOCVD reactor. (This reactor was built and put into use after the experiments presented in this thesis were completed.) First, the susceptor will be positioned on the top wall of the flow tube. Since the hottest region of the reactor is at the highest point, the density gradient resulting from the temperature gradient will be stable, and natural convection will be eliminated. Similarly, the fraction of
the density gradient that arises from concentration differences as the metalorganic species decompose at the surface will also be stable. Puetz, Hillier, and SpringThorpe (81) obtained good results for the growth of GaInAs and InP in an inverted horizontal MOCVD reactor. Gas phase nucleation problems will also have less effect on film quality since dust particles will settle away from the growth surface due to gravitational acceleration.

A second change in the reactor design will be to utilize a tube with rectangular cross-section (four to one width to height ratio) as the inner flow tube to allow relatively simple modeling of the gas flow in the reactor. The sidewalls of the reactor will have an effect on the temperature and flow profiles. Therefore, it is important to scale the aspect ratio of the reactor so the flow over the growth region is minimally disturbed by the boundary layer on the side walls. Van de Ven et al. (82) have determined experimentally that under typical laminar flow conditions in horizontal MOCVD reactors, an aspect ratio of four to one results in uniform growth laterally over 50% to 70% of the susceptor width. The gas flow over the central area of the cross section can be modeled as two-dimensional Poiseuille flow between parallel plates.

4.5 Exhaust System and Treatment

The exhaust system consisted of several particle filters, a pyrolysis furnace, adsorption trap and a corrosive service mechanical pump. To minimize pressure drop through the tubing, all tubing downstream of the reactor was 1/2 inch diameter stainless steel rather than 1/4 inch as was used for the upstream gas lines. All connections were either welded in house or sealed with
VCR fittings using silver plated nickel gaskets. The mechanical pump was rated for a 760 liter per minute displacement.

A great deal of solid particles are produced in the MOCVD reactor and at the outlet of the pyrolysis furnace. These solid particles must be removed from the gas or they could block the small orifice of the pressure control throttle valve. A bubbler immediately downstream of the reactor was filled with silicone diffusion pump oil (Corning D-705, 10^{-10} torr untrapped) to trap many of the particles formed in the reactor. The oil bubbler also prevented the inadvertent backstreaming of air into the reactor in case of a system failure during a growth experiment. An inverse bubbler trap was located immediately upstream of this bubbler to catch any oil that was forced upstream by pressure imbalances during nonflow procedures. A large area filter, downstream of the pyrolysis furnace, removed 93% of 0.1 μm size particles.

The exhaust stream was treated to remove unreacted metalorganic compounds and possibly toxic by-products before release to the atmosphere. Any unreacted metalorganic compounds were destroyed in a pyrolysis furnace, downstream of the reactor, kept at 850 °C. The pyrolysis furnace was constructed from a 24-inch long 304 stainless steel tube with a 1.5-inch outer diameter. Approximately twelve inches of the tube was positioned inside the clamshell furnace. Baffles, spaced approximately one inch apart, were attached alternately to two of three threaded rods in the heated section of the tube. The baffles were used to cause turbulent mixing of the gas in the furnace tube to ensure that the gas came into contact with the hot surface. Material built up inside the furnace tube with time and it was necessary to replace the tube after several months when the pressure drop across the tube became too great to
maintain the required reactor pressure under flow conditions. The subsequent furnace tube was filled with heavy copper turnings rather than baffles to add to the heated surface area.

Hydrogen selenide was a likely by-product of the MOCVD reaction and of the gas pyrolysis. A packed bed of potassium hydroxide impregnated charcoal was positioned in an adsorption trap at the inlet to the mechanical vacuum pump to remove this toxic gas. The hydride was oxidized by the caustic and adsorbed on the charcoal. A bed of activated alumina beads below the charcoal was also added to adsorb any hydrocarbon pump oil before it could backstream into the reactor system.

4.6 Control Panel - Valve Sequencer and Safety Interlocks

There were a total of 35 valves for gas switching in the LMOCVD apparatus. During an experiment, different configurations of valves were open at various stages of the growth procedure. Rather than operating each valve separately, a set of push button controls was designed for valve sequencing during typical growth procedures. Detailed wiring diagrams of the controller electronics are shown in Appendix B.

All shut-off valves in the system were normally-closed, air-operated stainless steel bellows valves which required an inlet pressure of at least 70 psig for operation. The air supply to each bellows valve was controlled by electrical solenoid valves. Power to operate the solenoids was provided by a 35 amp, 12 volt DC supply. The normally closed option on the bellows valves was chosen for safety considerations to prevent the opening of an unsafe
sequence of valves if there were a power failure. Upon loss of power, all valves close.

There were several safety interlocks that cause all of the valves in the system to close upon triggering of the interlock, effectively shutting down the process. Over-pressure in the reactor or either bubbler, detection of combustible gas in the enclosure or room, and a reduction in pressure of the air supply would result in a system shut down. Electrical signals from these devices were input through a differential amplifier comparator into a TTL circuit. If any of these signals deviated past a reference setpoint, an interlock was triggered that closes a relay which was in parallel with the valve sequencer select button that closed all valves in the system. An interlock bypass switch was located on the front panel, and could be used to bypass the interlock system in situations when it was necessary to operate the system to remedy an over-pressure problem.

The interlock relay was also used as a precaution during system power-up. The controller electronics were configured so that the relay closed when power was first applied to the controller ensuring that the system was latched into all-valves-closed mode. The reset button was then used before normal operation of the controller could be started.

4.7 Excimer Laser and Optical Components

A Questek Model 2420 excimer laser was used for these experiments. The excimer laser is a useful source of ultraviolet radiation. In such devices, a gas mixture of a rare gas (Ar, Kr, or Xe), a halogen (F or Cl) and a buffer, typically helium, are excited to a higher energy state by a high voltage
discharge. In this process, excited dimers (excimers) of the halogen and rare gas are formed which emit ultraviolet radiation during the electronic transition from the excited state to ground state. The wavelength of the laser radiation is determined by choice of the rare gas/halogen gas mixture in the laser cavity. The metalorganic compounds used for the growth of ZnSe have high absorption cross-sections at 193 nm, the wavelength of the excimer mixture containing argon and fluorine (ArF) (see Section 2.3). Therefore, ArF excimer laser radiation was used for the majority of the experiments. The laser was rated for pulse energies of 275 millijoules (mJ) at 193 nm. However, since the laser had been in operation for three years, the maximum output energy of the ArF mixture had decreased to approximately 200 mJ. This laser was capable of repetition rates up to 50 hertz. The approximate pulse duration was 15 to 20 nanoseconds full width half maximum.

The output energy of an excimer laser typically decreases with time of operation as impurities form in the gas and the gas mixture is depleted. The Questek 2420 was one of the first excimer lasers to have an on-board microprocessor. The microprocessor uses feedback from an energy detector and information from the keyboard panel to control the laser output. The output energy was measured by diverting a fraction of the laser beam to a photodetector using a quartz beamsplitter. The output from the detector was then fed back to the microprocessor, which controlled the high voltage power supply to maintain constant output energy (±5 mJ) as set at the keyboard. This output power control was possible up to the maximum high voltage value of 23 kV. The ArF gas fill is very short lived compared to other excimers. A cryogenic trap was made to extend the lifetime of the ArF excimer gas fill by
condensing out impurities in the gas in a liquid nitrogen trap. The gas lifetime increased from 15 minutes to several hours of operation at 20 hertz with 100 mJ output energy. Typical growth experiments lasted from 0.5 to 1.5 hours and therefore the cryogenic trap was essential to maintain constant output throughout the duration of each experimental run.

The laser beam was directed toward the side window of the reactor by two beam-steering mirrors. These mirrors were coated with a dielectric for maximum reflectance of 193 nm radiation at a 45° incidence angle. The beam was then partially focused through the reactor with a fused silica lens (f = 250 mm). Experiments were done with the excimer laser radiation either incident on the GaAs substrate surface or just above and parallel to the growth surface. For parallel experiments, the radiation passed above the substrate surface in a region approximately 1 cm by 0.35 cm in cross section at the center of the reactor. For incident experiments, the substrate holder was rotated ~30° so that the laser radiation fell on the substrate directly. Energy losses at the mirrors, lens, window and by absorption in air were approximately 50%.

The reactor system described above in chapter 4 was designed and built in a Rice University laboratory over the period from 1986 to 1988. ZnSe epitaxial films were successfully grown on (100) GaAs substrates by both conventional and laser-assisted MOCVD. The experimental procedures and results are presented in the next two chapters.
Chapter 5
Experimental Procedures
and Film Characterization Methods

ZnSe film deposition was accomplished in the LMOCVD reactor system that was described in Chapter 4. Experiments to examine the effect of several laser parameters, temperature, and other reactor conditions on film deposition rate and quality were done. This chapter contains a detailed description of the experimental procedures and film characterization techniques that were used during these experiments.

5.1 Experimental Procedures

Substrate Preparation

Two inch diameter (100) GaAs wafers, oriented 2° toward the <110> direction, were purchased from a commercial vendor. The wafers were grown using the Czochralski technique and had a bulk electrical resistivity greater than $10^7$ ohm-cm. Each wafer was polished on one side and was approximately 360 μm thick. Using a diamond-tipped scribe, the wafers were cleaved into approximately 12.5 mm by 12.5 mm squares. However, since the wafer was circular, the resulting pieces varied somewhat in shape.

Substrate cleanliness is extremely important for epitaxial growth. Many substrates were chemically cleaned prior to introduction to the reactor. The substrate was chemically etched in a $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2$ (30%) : $\text{H}_2\text{O}$ solution (6:1:1 by volume) for 30 seconds at a temperature between 40 °C and 50 °C, flushed
for one minute in de-ionized water and blown dry with filtered nitrogen. The substrate was then immediately attached to the heater, dusted off again with filtered nitrogen and positioned in the center of the reactor. The wet cleaning procedure was found to adversely effect film growth for some films, and in most experiments the wet cleaning procedure was omitted.

**Substrate Loading and Sample Removal After Deposition**

The introduction of a new substrate and the removal of the previous sample were performed during one procedure. This minimized the total number of times that the reactor was opened to the atmosphere and that the operator was exposed to selenium and its compounds. The overall procedure consisted of several steps.

1. Post-deposition hydrogen purge until $T_{\text{Sub}}$ was less than 30 °C.
2. 4 cycles of reactor pump-out followed by a helium back-fill.
3. Opening the reactor.
4. Removal of previous growth followed by mounting of cleaned substrate.
5. Inserting heater and re-sealing of the reactor.
6. 4 cycles of reactor pump-out followed by a helium back-fill.
7. Pre-deposition hydrogen purge.

After a growth experiment the reactor was purged with hydrogen carrier gas for a minimum of one hour to remove any unreacted metalorganic compound or by-product that might remain in the reactor, as well as to allow the substrate to cool down to near room temperature before opening the reactor to air. The hydrogen flow rate and reactor pressure used during the purge were
the same as during the growth experiment (1000-2000 sccm hydrogen and 100-300 torr respectively). After the purge was complete and the substrate was cool, further dilution of any remaining hazardous vapors was achieved by pumping the reactor down to a pressure of 300 mtorr or less followed by subsequent backfill to greater than 800 torr of helium. Repeating this procedure four times resulted in an estimated dilution factor within the reactor of better than $10^{-11}$.

Protective clothing and respiratory apparatus were used during all steps of the procedure where the reactor was open to the atmosphere or contact with contaminated surfaces could occur (steps 3-5 above). For protective clothing, a laboratory coat, along with disposable Tyvek™ sleeve covers and either polyvinyl or latex gloves were worn. Respiratory protection was initially through use of half-mask respirators with cartridges designed to filter out metal fumes. However, we later improved this aspect of protection through the use of a face-shield and hood which was supplied with clean air from an area outside the laboratory.

After taking the above safety precautions, the reactor could be opened for the exchange of substrates with minimal exposure to selenium contamination. The following procedures were followed for removing and changing substrates. The leads to the back of the end-flange for both the thermocouple and the heater were disconnected from their feed-throughs. The bolts which held the end-flange on to the reactor were then removed. Finally, the Ultra-torr™ O-ring compression fittings on the flexible tubing connecting the back flange to the vacuum system were disconnected and the entire section, including the flange and the heater, were separated from the reactor. The heater was supported by
the exit cone of the reactor while the substrates were exchanged. In order to remove the substrate from the heater, one end of the stainless steel mounting clip was carefully lifted and the substrate was rotated out from under it. The other end of the clip was then lifted and substrate removed and placed in a plastic wafer tray to await later analysis.

After a number of growth experiments the substrate heater became coated with ZnSe and other deposition products. Eventually this material would become so thick that it would start to flake off the heater and could contaminate subsequent growths. Therefore, the heater was inspected each time it was removed, and replaced with a clean heater when the deposited film appeared to be getting too thick. This problem also occurred with the substrate mounting clip, but was somewhat more severe as the flexing of the clip during substrate change tended to dislodge particles more readily. As a result the clip was exchanged more frequently than the heater itself.

Following the heater inspection, a new substrate was then chemically cleaned (see previous section) and carried to the reactor immersed in de-ionized water. The substrate was blown dry with filtered nitrogen gas and carefully positioned under the clips on the heater. Substrates which did not undergo chemical etching, were simply transferred from the storage box to the heater. Fragments of material would often flake off the clip during the mounting procedure and land on the substrate. Therefore the substrate was given a final dusting off with dry nitrogen before carefully inserting the heater into the reactor. A final check of the thermocouple position and the integrity of heater leads was also made prior to insertion. The end flange was then resealed and tightened.
evenly. The O-ring compression fittings were then connected and tightened finger tight and the electrical and thermocouple connections remade.

Before any protective clothing was removed care was taken to clean up particles that may have fallen off near the reactor. These particles were cleaned up with a damp Kimwipe tissue, which was then disposed of, along with the gloves and sleeves, in metal cans. These cans were sealed when full, and labeled for disposal by a hazardous waste disposal service.

Prior to deposition the reactor was evacuated and refilled with 800 torr of ultrahigh-purity helium. This cycle was repeated four times to remove air and water vapor, which had entered the reactor during the substrate exchange. Then the system was purged with hydrogen for a minimum of 30 minutes at a flow rate of 2000 sccm and a reactor pressure of 100 torr. These precautions were necessary because of the pyrophoric nature of both DESe and DMZ as well as for reliable film purity.

**Pregrowth Procedures**

The importance of sufficient purging of the reactor prior to film growth was mentioned in the previous section. The repeated evacuation of the reactor followed by helium backfill was accomplished by manual sequencing of the electrical control valves. The chamber was left at a pressure of several hundred millitorr at the end of this procedure. At this point, the tubing downstream of the reactor was also evacuated by selection of mode 3 of the valve controller. This prevented the possibility of a reverse pressure gradient across the oil bubbler trap, which would suck the oil out of the trap back towards the reactor. A hydrogen purge was then initiated by selection of mode 4 which caused
hydrogen to flow through all window purges, the outer tube purge lines, the
bubbler by-pass and carrier gas lines. This hydrogen then passed through the
reactor and out through the pyrolysis furnace and vacuum pump. Nitrogen from
the blow-off of a liquid nitrogen storage tank was introduced into the gas stream
at the outlet of the pump through a separate valve to dilute the hydrogen to
prevent combustion as it is vented to the atmosphere. Because the initial
pressure downstream of the mass flow controllers was that of the supply
regulators (about 30 psi), mode 4 also opened valves which by-pass the bubble
throttle valves. If this was not done, the pressure at the Baratron gauges which
monitored the bubbler pressures would exceed their safe operating limit. After
the initiation of hydrogen flow, the pressure in the bubbler by-pass lines quickly
fell to a safe level. Once the pressure in the bubbler lines was decreased, the
system was changed over to purge mode 5 which closed the throttle valve by-
pass and allowed the pressure in the bubbler lines to rise to 760 torr. The
reactor was purged for a minimum of 30 minutes at a pressure of 100 torr and a
flow rate of 2000 sccm.

The final step before growth was an in situ thermal etch to remove the
native oxide from the gallium arsenide substrate. The native oxide on GaAs is
thermally desorbed at temperatures of about 530 °C under vacuum, but
researchers typically heat the substrate to between 600 °C and 630 °C for a few
minutes to ensure removal of the native oxide. (83) Most of the work reported
here used a three minute etch at 590 °C to 620 °C at a pressure of 100 torr in
1000 sccm flowing hydrogen. The substrate temperature was gradually raised
to the etch temperature over a period of about 12 to 15 minutes by slowly
incrementing the Variac autotransformer output voltage which supplied power
to the substrate heater. Once the desired etch temperature was achieved, it was controlled by small adjustments of the voltage.

At the end of the etch period (about three minutes) the power to the heaters was shut off so that the substrate could quickly cool to the desired growth temperature. While the substrate was cooling, the pressure and flow rates were adjusted to the values which would be used during the growth of the ZnSe film. The heater voltage was then adjusted to achieve the desired growth temperature with a stability of ±2 °C.

The reactor system was allowed to thermally stabilize at the desired substrate temperature for at least five minutes and usually about 15 minutes before any metalorganic was introduced. To assure proper laser positioning above the substrate, the excimer laser beam was aligned during the time that the reactor was stabilizing. The image of a low power (50 mJ, 10 Hz) laser beam passing through the laser cell was used to achieve proper alignment. The beam was adjusted with the focusing lens and second dielectric mirror such that beam was parallel to, and just above, the surface of the substrate.

**Epitaxial Film Growth**

Epitaxial growth was initiated only after the pre-growth procedures mentioned above were completed. When the substrate temperature had stabilized for at least five minutes, the excimer laser was turned on at the required pulse energy and repetition rate. Then, the flow of metalorganic source gases was initiated by switching the flow of carrier gas to the bubblers. Selection of mode 6 of the valve sequencer opened valves 12, 13, 18 and 19, equalizing the pressure upstream and downstream of the bubblers (see Figure
4.3.1). The manual shut-off valves on both bubblers were then opened without the risk of loss of metalorganic from the bubbler due to an inadvertent reverse pressure gradient. The diethylselenide bubbler shut-off valves were opened first to ensure an excess of the selenium source, even if any metalorganic was transported to the reactor before the bypass valves were closed. Next, mode 7 of the valve sequencer was selected to close both bubbler bypass valves (14 and 20), beginning the flow of carrier gas through the bubblers. The deposition time was measured for later determination of film growth rate.

A set of standard reactor and flow conditions was used for a large number of the growth experiments. The reactor was normally operated at a pressure of 100 torr with a total flow rate (excluding various purge flows) of 2000 sccm. The metalorganic sources were transported at a 10 to 1 DESe to DMZ ratio with flow rates of 25 sccm and 2.5 sccm respectively. This set of conditions resulted in a 1.25 torr DESe partial pressure and 0.125 torr DMZ partial pressure in the reactor. The laser was operated at 20 Hz with a pulse energy of approximately 50 mJ, and was partially focused through the reactor to a spot size approximately 1 cm by 0.35 cm in cross-section at the center of the substrate.

Film growth was monitored in situ by the time-resolved reflectivity (TRR) of a HeNe laser beam off the growth surface. (17) The laser beam was partially reflected at the ZnSe surface and at the ZnSe/GaAs interface. As the film thickness changed, the degree of interference from the recombination of these two light beams oscillated. The intensity of the reflected laser beam was detected using a photodiode, and recorded as a function of time on a strip chart recorder.
In the time-resolved reflectivity plots, each cycle from maximum reflectance to maximum reflectance indicated an increase in film thickness of \( \lambda/2n \). (17) The refractive index of ZnSe at 632.8 nm is approximately 2.6. (84) Therefore, each cycle represented a change of 0.12 \( \mu \text{m} \) in film thickness. A perfect ZnSe crystal would not absorb HeNe laser radiation; however, the amplitude of the TRR signal decreased with film thickness, probably due to defects in the film. The relative change in TRR amplitude was, therefore, an indication of film quality, as well as a method to

![Graph showing film thickness vs. TRR cycles.](image)

**Figure 5.1.2.** MOCVD ZnSe film thickness by interferometry versus time-resolved reflectance (TRR), one TRR cycle equals 1200 Å.
measure growth rate. Film thickness was later verified using an interferometric technique (see Section 5.2). Figure 5.1.2 is a comparison of the ZnSe film thicknesses measured experimentally by interferometry and TRR. There is excellent agreement between the measurements using both techniques, except for film thicknesses greater than 1 μm. The film thickness measured by interferometry was used to calculate growth rate, however, since a value for the refractive index must be assumed to calculate thickness by TRR.

The progress of the film growth was followed using the TRR measurements and stopped at the desired thickness. Mode 6 was again selected and the manual valves on the bubblers closed (DMZ first). Then, upon selection of mode 5, hydrogen was allowed to purge the reactor. The laser was turned off immediately after this valve sequencing was completed, but the substrate heater temperature was maintained for one more minute so that if any further growth were to occur it would be at the correct growth temperature. Then, the heater power was turned off and the substrate allowed to cool in hydrogen flow.

Furnace Tube Maintenance

Unreacted metalorganics from the reactor, as well as reaction products were destroyed in a pyrolysis furnace located between the reactor and the vacuum pump. Zinc, selenium and carbon would build up on the copper turnings in the cooler regions near the outlet to the furnace tube. This build-up reduced the conductance through the furnace and result in an increase in the pressure drop across the furnace tube. Eventually the pressure drop would increase until it was impossible to maintain the reactor pressure at 100 torr or less, at which point it was necessary to replace the furnace tube. After allowing
the furnace to cool overnight, the furnace was purged with helium several times
to be sure all pyrophoric gases had been removed from the system. The
Conflat connections on either side of the tube were removed, one at a time, and
replaced with blank flanges. The tube was then placed in a double plastic bag
and stored for later disposal. Care was taken throughout this procedure to wear
proper protective clothing and air supply hoods, and plastic and other materials
were used to contain the furnace products in the tube.

5.2 Film Analysis Methods: Thickness, Photoluminescence and
Electrical

Film Thickness Measurement and Morphology Observations

The morphology of the ZnSe films was examined immediately after
growth both by eye and with Nomarski differential interference contrast
microscopy. Immediately after removing the grown film from the reactor, the
interference fringe pattern was observed by eye for an indication of relative film
uniformity. The specular or "cloudy" appearance of the film gave an indication
of surface roughness. The films were then examined using the Nomarski
microscope at a magnification of 500 times to determine the presence of gross
film defects such as large inclusions or pits, and other morphological features.
The depth of field using Nomarski microscopy is much greater than for
conventional reflected light microscopy, and therefore, surface features such as
hillocks or shallow pits could be resolved. The morphology of the ZnSe films
was documented by photographing the films under the Nomarski microscopy at
500X magnification. After the morphological observations were complete, the
samples were cleaved with a diamond-tipped scribe. A section of relatively uniform film thickness, i.e. grown under the laser beam, was set aside for photoluminescence analysis and electrical measurements, while fragments of the wafer from areas adjacent to this region were used to determine film thickness.

Film thickness was measured using an interference objective on an optical microscope to determine the step height from the ZnSe layer down to the GaAs substrate. Parts of the films were first painted with black wax and then the uncoated areas of the ZnSe film were etched down to the GaAs substrate using a hydrogen peroxide solution (30% in water). After removing the black wax with trichloroethylene solvent, the film was flushed in acetone and methanol and dried with a gentle spray of pressurized freon. A sharp step from the ZnSe film to the bare GaAs substrate was then present where the edges of the black wax had been. Identical chemical processing of the GaAs substrate was done to study the etch rate of GaAs; no measurable etching occurred in any GaAs substrates even after a period of twenty-four hours in the hydrogen peroxide solution.

Typical etch times for the ZnSe films were from one to five hours. The uncoated films turned green initially during the etch, and could eventually be flushed away using deionized water. Although a thin black residue often remained on the surface after the etch, most of the film was totally removed. The thinnest ZnSe films were often the most difficult to etch away, and usually a thin residue remained over the entire wafer.

The height of the etched ZnSe / GaAs step was measured using a Watson-Barnett 16 mm interference objective on an optical microscope. The
measurement technique is based on the light interference that results after two parts of a light beam recombine after traveling different distances. Constructive interference occurs if the optical path lengths differ by a full wavelength, whereas destructive interference occurs if the paths differ by a half wavelength. Light enters the interference objective from the side, and is split by a beam splitter prism into two parts (see Figure 5.2.1). One beam passes through the beam splitter prism, is reflected off a reference mirror back to the beam splitter prism, where it is reflected up toward the microscope eyepiece. The other light beam is reflected toward the sample, then reflected off the surface and back up through the beam splitter prism, where it recombines with the reference beam.

![Diagram](image)

Figure 5.2.1. Schematic of film thickness measurement by interferometry.
The interference fringe pattern that arises is essentially a topographical map of the film surface. Since the reference beam path is parallel to the film surface, straight line fringes will appear for interference off a flat surface. Changes in film thickness across the surface are seen as a lateral shift in the fringe pattern, a shift of one fringe spacing occurring for each half wavelength change in thickness for monochromatic light.

Gradual changes in film thickness are observed as continuous shifts in the fringe pattern. However, wet etching of the films resulted in a sharp step which causes a discontinuity in the fringe pattern. Because of the sharp step, it was often difficult to determine accurately the magnitude of the overall shift in the fringe pattern for shifts greater than one fringe. To overcome this difficulty, white light fringes were used. The white light interference fringe pattern has one central black fringe which is clearly distinguishable from the colored fringes. Film thickness measurements were made using white light and monochromatic fringes in the following manner. First, the interference reference mirror was adjusted to obtain monochromatic light interference fringes. Monochromatic light was obtained by passing white light through a mercury line interference filter at 5461 Å. Next, the filter was removed and white light fringes examined. The image of the fringe pattern was collected with a television camera and shown on a 13-in. black and white television monitor. The displacement D of the central white light fringe was measured on the television screen to within 0.05 inches using a ruler. Then the green filter was reinserted and the number of monochromatic fringes per distance on the television screen were measured by measuring the displacement across several fringes. The film thickness t was then calculated by the equation
\[ t = D \frac{N \lambda}{L} \]  \hspace{1cm} (5.2.1)

where

\[ N = \text{number of monochromatic fringes} \]
\[ L = \text{displacement on television monitor for } N \text{ monochromatic fringes (inches)} \]
\[ \lambda = 0.5461 \mu \text{m} \]

The inherent measurement error was approximately 500 Å due to errors in measuring fringe spacing on the television monitor. However, this error was negligible compared to the errors introduced by variations in the etching of the films which could bring about an error of approximately 2000 Å for the thicker films, or about 10% of the overall thickness.

**Photoluminescence Analysis**

Photoluminescence analysis of the LMOCVD grown ZnSe films was used to examine film quality. Samples were cleaved approximately in half with a diamond-tipped scribe. One section was used to obtain a film thickness measurement (see previous section) while the other section was first analyzed using photoluminescence and then, for later experiments, characterized electrically using the van der Pauw Hall technique (see next section). The photoluminescence analyses were done at the Texas Instruments Inc. Central Research Laboratory in Dallas, Texas. A schematic of the apparatus is shown in Figure 5.2.2. A 1.5 mW helium-cadmium laser supplied 325 nm radiation as the excitation source. The laser radiation was directed in through the side window of a helium Dewar chamber by two aluminum mirrors and partially
Figure 5.2.2. Schematic for photoluminescence apparatus.
focused onto the zinc selenide film using a fused silica lens \((f = 100 \text{ mm})\). The radiation emitted from the zinc selenide film was collected with a glass lens and focused onto the slit of a 0.8 m scanning spectrometer. The light was detected by a GaAs photomultiplier, cooled to liquid nitrogen temperature to minimize noise.

For photoluminescence, the ZnSe films and a GaAs standard were secured to the copper stage of a helium Dewar with small drops of rubber cement. The stage was lowered into the Dewar which was then evacuated prior to admitting liquid helium. Each sample was cooled to 4.2 K by submerging part of the cold finger in liquid helium immediately before each photoluminescence spectrum was collected. The spectrometer was calibrated each day to within 0.05 Å on the 5400.6 Å line from a neon calibration lamp and verified on the 8187 Å exciton line from the photoluminescence of the GaAs standard cooled to 4.2 K.

Low resolution spectra were collected for each ZnSe film over the wavelength range from 4350 Å to 6350 Å by scanning the spectrometer over this range at 5 Å increments \((3 \text{ meV resolution})\). The corresponding energy range is 2.85 to 1.95 eV. The presence of donor or acceptor bound-exciton emission, donor-acceptor pair recombination and deep centers were determined by analysis of the spectra. The resolution of these scans was insufficient to identify specific impurities, but this strategy allowed time for the analysis of a greater number of samples over this large wavelength range. The photoluminescence spectra could be used as a measure of film quality by comparing the relative intensity of the emission from neutral donor-bound
excitons to that for the self-activated emission near 2.05 eV which has been associated with lattice defect (vacancies) impurity centers. (52)

Higher resolution photoluminescence spectra between 4350 Å to 4850 Å were collected from selected ZnSe films cooled to 1.6 K. Such spectra are needed to identify impurity species from the energy level of the bound-exciton emissions. The spectra were collected by time-averaging the emission signal over five wavelength scans, sampling at 0.5 Å increments for a resolution of 0.3 meV. Unfortunately, the excitonic emissions for different donor species are separated by only tenths of an meV, and therefore, the exciton emissions could not be assigned to a specific impurity, but a number of possible species could be identified.

**Electrical Characterization - Van Der Pauw Hall Measurements**

Van der Pauw Hall measurements (85) were made on selected samples of the epitaxial ZnSe films in order to determine carrier concentration, type (n or p) and mobility. A Hall sample of dimensions from 0.25 cm² to 1 cm² was scribed from the central section of the substrate where the thickness of the epitaxial films were most uniform. Electrical contacts were formed by pressing small pieces of indium (99.985% pure) onto the corners of the sample. These contacts were then annealed at 300 °C for 5 to 10 minutes in a reducing atmosphere of 4% hydrogen in nitrogen (forming gas). The sample was then mounted on a ceramic integrated circuit (IC) package using silicone rubber in order to hold it in place.

Gold leads were then soldered between the pins on the IC package and the indium contacts. Care was taken to ensure that the contact width did not
exceed 1/8 of the sample dimensions in order to minimize measurement error. The IC package was wrapped with two layers of Teflon tape (poly-tetrafluoroethylene) for electrical insulation and plugged into a socket on the end of the sample positioning rod. The IC package, socket and rod were covered with more tape and then a layer of aluminum foil. The foil acted as a light barrier to eliminate photocurrent effects, as well as to shield the sample from electrical interference. The rod was lowered into a glass Dewar flask which was positioned between the poles of an electromagnet with the sample oriented perpendicular to the direction of the magnetic field.

The resistivity \( \rho \) of the sample was determined in the following way. A current of approximately 50 \( \mu \)A was applied sequentially across adjacent contacts in configurations A through D as shown in Figure 5.2.4. The voltage between the two other contacts in each configuration was measured with a digital voltmeter. The film resistivity was then calculated using the equation

\[
\rho = \frac{\pi \cdot t \cdot f \left( \frac{R_A + R_B}{2} \right)}{\ln 2}
\]  

(5.2.2)

where

\[ t = \text{film thickness (cm)} \]

\[
R_A = \frac{V_A}{I_A} + \frac{V_C}{I_C}
\]  

(5.2.3)

\[
R_B = \frac{V_B}{I_B} + \frac{V_D}{I_D}
\]  

(5.2.4)

\[ f = \text{a function of } R_A/R_B \text{ (depends on sample geometry).} \]
Hall measurements were made using configurations E and F as shown in Figure 5.2.5. Here current of about 50 μA was allowed to flow from one corner of the sample to the other. The voltage between the other two contacts was measured with and without the magnetic field applied perpendicular to the sample. This measurement was repeated with the magnetic field oriented in the opposite direction. Then the entire procedure was done again, with the contacts reversed. The difference in voltage, with and without magnetic field,
was averaged for the two directions of field for both configurations, E and F, and normalized to the current used for each measurement. These two values were averaged, in order to minimize errors due to non-symmetry of the contacts, as shown below:

\[ \Delta R_0 = \frac{\left( \frac{\Delta V_f + \Delta V_r}{2I_E} \right)_{E}}{2} + \frac{\left( \frac{\Delta V_f + \Delta V_r}{2I_F} \right)_{F}}{2} \]  (5.2.5)

Where \( \Delta V_f \) is the change in voltage with and without the magnetic field applied in the forward direction, while \( \Delta V_r \) represents the same change, but with the field in the reverse direction.

The carrier mobility, \( \mu \), could be calculated using the equation:

\[ \mu \left( \frac{\text{cm}^2}{\text{V s}} \right) = \frac{10^8 \Delta R_0 t}{B \rho} \]  (5.2.6)

where \( t \) is the film thickness (cm) and \( B \) is the applied magnetic field in Gauss. (85)

Carrier concentration, \( N_d \), could be determined from the mobility \( \mu \) and resistivity \( \rho \) by using the following:

\[ N_d = \frac{1}{(\rho \; q \; \mu)} \]  (5.2.7)

with \( q \) being the charge of an electron, 1.6 x 10\(^{-19}\) C. (85) These measurements were made at both room temperature and 77 K, the latter was accomplished by adding liquid nitrogen to the dewar and submerging the sample.
Chapter 6
Results and Discussion

The results of the experiments examining the effects of substrate temperature and laser power density, repetition rate and beam orientation are reported in this chapter. The observed dependences of growth on the reactor variables of total and partial pressures and flow rates are also presented. Film quality, as determined by the morphology and photoluminescence, are examined. The mass spectral analyses of gaseous reactor products are reviewed.

6.1 Effect of Substrate Temperature on ZnSe Film Growth

The effects of temperature on MOCVD ZnSe film growth were examined for both thermally and laser-assisted film growth. As specified in section 5.1, the temperature effect was studied for only one standard set of reactor conditions which were as follows: Reactor pressure = 100 torr, DMZ flow rate = 2.5 sccm, DESe flow rate = 25 sccm, total flow rate = 2000 sccm, ArF excimer laser operated at 20 Hz, pulse energy = 50 mJ. The effects of temperature on growth rate, morphology and photoluminescence were then analyzed.

The dependence of growth rate on substrate temperature for both MOCVD and LMOCVD processes is shown in Figure 6.1.1. Data for this figure were derived from film thicknesses measured interferometrically. No measurable growth was observed in thermally deposited films for temperatures below 425 °C. The growth rate increased from 0.2 μm/hour at 425 °C to
4.4 μm/hour at 550 °C. With laser-assisted growth, however, material was
deposited at a nearly constant rate of about 1 μm/h from 200 °C to 400 °C.
Material deposited at 100 °C did not coalesce into a film. At temperatures
greater than 400 °C, thermal growth occurs and begins to dominate film growth
above 500 °C. The estimated error in the thickness measurements was about
10%, meaning that the growth rates by both MOCVD and LMOCVD at
temperatures greater than 500 °C are essentially the same.

![Graph showing growth rates vs. temperature for MOCVD and LMOCVD growth of ZnSe.]

Figure 6.1.1 Growth rates versus temperature for thermally-activated (MOCVD)
and laser-assisted (LMOCVD) growth of ZnSe.
Assuming a thermally-activated growth rate of the form
\[ \text{Rate} = \text{Rate}_0 \, e^{-(E_A/RT)} \]  
(6.1.1)

one can determine the activation energy \( E_A \) by measuring the slope in a
Arrhenius plot of the natural log of the growth rate versus inverse temperature.

Figure 6.1.2 Arrhenius plots of ZnSe growth rate versus temperature for this
work; thicknesses measured by interference and time-resolved
reflectivity (TRR) methods.
The measured rates of thermally driven MOCVD as determined from the interferometric and time-resolved reflectivity (TRR) thickness measurements are plotted versus reciprocal temperature in Figure 6.1.2. The measurements are in good agreement for the thermally grown films. Calculated activation energies were 30 and 32 kcal/mol from the interference and TRR measurements,

![Figure 6.1.3 Arrhenius plots of the growth rate versus temperature for thermally activated (MOCVD) and laser-assisted (LMOCVD) growth of zinc selenide.](image-url)
respectively. The Arrhenius plots of the laser-assisted and thermal processes are shown in Figure 6.1.3. These rate data are both derived from interference measurements of the film thicknesses.

The morphologies of the deposited films were examined using an optical microscope with Nomarski differential interference contrast enhancement. A scanning electron microscope was also used to examine the surface quality of some of the films. An attempt to deposit a film at 100 °C using LMOCVD resulted in a black powdery deposit. Figure 6.1.4 is an SEM photomicrograph of this film. Particles (presumably ZnSe, zinc or selenium) 10 µm or less in diameter condensed on the substrate surface. However, the particles had not coalesced into a single film at this substrate temperature. For growth

![SEM photomicrograph](image)

**Figure 6.1.4** SEM photomicrograph of a film deposited at 100 °C using LMOCVD.
Figure 6.1.5. Nomarski photomicrographs of ZnSe films grown at a) 400 °C and b) 500 °C by LMOCVD. (scale = 100 μm)
temperatures of 200 °C or higher, the films were generally specular. Nomarski photomicrographs of LMOCVD films grown at 400 °C and 500 °C are shown in Figure 6.1.5. At the magnifications used here (475X) only a small amount of surface roughness is apparent. Overall uniformity of the deposited films could be estimated from the interference fringes in the films when they were observed in daylight. In thermally deposited films, most of the surface was of uniform thickness except near the regions where the mounting clips contacted the film. In laser-assisted films, the region of uniform (enhanced) growth was about 0.5 cm wide extending across the substrate in the direction of the laser beam propagation.

The quality of selected ZnSe films from the temperature dependence study was examined using photoluminescence (PL) analysis at 4.2 K. Figure 6.1.6 shows the PL spectra of LMOCVD ZnSe films grown at 200 °C, 400 °C and 475 °C. The PL spectra of all of the films analyzed were dominated by the self-activated (SA) emission near 2.1 eV. This broad transition has been associated with zinc vacancies and their associated impurities (see section 3.3). The PL spectrum from the LMOCVD film grown at 400 °C exhibited strong donor-bound-exciton emission at 2.799 ± 0.002 eV. The donor-bound-exciton luminescence intensity from this film exceeded that of all films examined in this study. The film grown at 200 °C had only weak self-activated emission and no evidence of any excitonic transitions. Films grown at temperatures of 500 °C and above all exhibited poor PL characteristics with strong self-activated emission and little or no excitonic activity. The LMOCVD ZnSe film grown at 475 °C exhibited luminescence from the neutral donor-bound exciton (I2) at 2.799 ± 0.002 eV and either the acceptor or ionized donor-bound-exciton
Figure 6.1.6. Photoluminescence (PL) spectra at 4.2 K of LMOCVD ZnSe films grown at a) 475 °C, b) 400 °C and c) 200 °C.
emission at 2.793 ± 0.02 eV. Weak emission from donor-acceptor pair recombination in the energy range from 2.75 to 2.6 eV and deep transitions at 2.60 eV (Y) and 2.5 eV (S) were also evident. These same transitions were also observed from the PL spectrum of a film grown thermally at 475 °C. The ratio of the neutral donor-bound exciton (l2) emission to that of the self-activated (SA) emission for the thermal films was greater than that for the laser-assisted film.

Discussion

Arrhenius plots for MOCVD growth of ZnSe from DMZ and DESe by Mitsuhashi et al. (34), this work and Giapis et al. (35) are shown in Figure 6.1.6. The measured activation energy of Mitsuhashi was 22 kcal/mol from depositions at 300 torr and a Se to Zn source ratio of two to one, whereas, Giapis determined 16 and 40 kcal/mol at 300 and 30 torr, respectively. Yamasaki et al. (86) measured an activation energy of 29 kcal/mol for ZnSe growth from DMZ and DMSe. Our measurement of about 30 kcal/mol compares well with these other published results.

The pressure dependence of the activation energy observed by Giapis is important and, as he points out, indicates a complex growth mechanism that most likely contains both gas phase and surface reactions. The MOCVD growth process consists of a series of steps, including mass transport, gas-phase processes, surface processes and possibly reactions between gas-phase and surface-adsorbed species. (see section 2.4) There may also be parallel reactions occurring simultaneously. For growth processes with a series of steps, the slowest step controls the overall reaction rate, whereas the fastest
step controls the overall rate for parallel reaction pathways. The relative importance of these different process steps may change for different reactor conditions, and therefore the apparent activation energy may change as a function of temperature or pressure. For instance, the reactor design may also have an effect on.

Mitsuhashi et al. (34) examined the growth rate of ZnSe for several combinations of source molecules, and found that the basic features of the Arrhenius plots were the same. The reaction rate is constant at temperatures above 500 °C, indicating a mass transport limited mechanism. At temperatures below 500 °C the reaction appears to be kinetically controlled, with activation energies of 22 to 24 kcal/mol independent of source combination. Mitsuhashi compared this behavior to that for GaAs MOCVD which is carried out in an excess of AsH₃ leading to a growth rate limited by Ga source transport. Since ZnSe growth is typically carried out using excess Se source, the film growth is likely limited by the transport rate of the Zn source at higher temperatures. Giapis et al. observed a similar behavior for the DMZ/DES system for depositions at 30 torr and 300 torr, but the onset of mass transport limitation occurred at a slightly higher temperature for the lower pressure process. There was no indication of mass transport limitation of the growth rate in our study, although scatter in the data could account for this.

The growth rate of ZnSe by LMOCVD was nearly constant at 1 μm/h over the wide temperature range from 200 °C to 400 °C (see Figure 6.1.3). The very low activation energy of the process meant that film deposition could be accomplished at various temperatures without sacrificing rate. However, the
results of the photoluminescence analysis indicated that film quality was poor for films deposited at growth temperatures less than 400 °C.

![Arrhenius plots of thermally-induced ZnSe growth from this work, Mitsuhashi et al.(34), and Giapis et al. (35)](image)

Figure 6.1.7 Arrhenius plots of thermally-induced ZnSe growth from this work, Mitsuhashi et al.(34), and Giapis et al. (35)

The ratio of neutral donor-bound-exciton emission to self-activated emission in the photoluminescence spectra is a measure of defect concentration. The low value for laser-assisted films grown at 475 °C, suggests that laser-assisted growth may degrade the quality of the deposited films. The
LMOCVD film grown at 200 °C was of very poor quality, and may not be crystalline. However, the film grown at 400 °C by LMOCVD had the highest quality, with better photoluminescence characteristics than even the films grown thermally at 400 °C. Apparently the thermal energy of the surface species was sufficient for good epitaxy with a one μm/hour growth rate at 400 °C but not at 200 °C. A reduction of the growth rate by decreasing source gas concentration, for example, may improve the quality of films grown at lower temperatures.

The transition energy levels for different donor-bound excitons in ZnSe are separated by only a few tenths of an meV. Therefore, the impurities responsible for the bound-exciton transitions can not be determined from these spectra, which are limited to a resolution of about 3 meV. The donor-bound exciton at 2.799 eV could be due to either gallium, aluminum or chlorine, which are all associated with transitions at 2.8002 eV. (68) The emission at 2.793 eV could be due to the acceptor-bound excitonic transition of sodium or lithium at 2.7930 and 2.7921 eV, respectively, or the ionized donor-bound excitonic transition at 2.796 eV of chlorine or indium. The Y and S transitions have been attributed to dislocations and their associated impurities in ZnSe MOCVD films, and their presence has been found to be dependent on both reactor cleanliness and growth temperature. (70) Gallium may be the impurity associated with these transitions since the rate of gallium out-diffusion from the GaAs substrate increases with temperature.
6.2 The Effect of Laser Power Density and Repetition Rate on ZnSe Growth

The effects of laser power density and repetition rate on laser-assisted MOCVD growth of ZnSe were examined. Thin films of ZnSe were grown by LMOCVD using four different pulse energies (15, 28, 38 and 48 mJ per pulse) at both 20 Hz and 40 Hz repetition rates. The growth temperature was kept constant at 425 °C, where thermal growth is negligible compared to that due to the laser assisted process. The standard conditions specified in section 5.3 were used for all flow rates and pressures. A 30 minute growth time was used for all growth experiments.

The growth rate of LMOCVD ZnSe is shown as a function of laser pulse energy and repetition rate in Figure 6.2.1. The ZnSe growth rate was nearly a factor of two greater using a 40 Hz repetition rate as opposed to the 20 Hz rate, which indicated the metalorganic concentration in the irradiated volume above the substrate was replenished in between laser pulses even at 40 Hz.

Assuming a Poiseuille flow profile in the reactor, a maximum linear flow velocity of approximately 10 cm/sec can be estimated for the region above the substrate. The actual flow rate will be lower because of the formation of a boundary layer along the surface. This would result in replenishment of only one quarter of the irradiated volume in the time between pulses at 40 Hz. Calculations in section 4.4 indicated that natural convection effects on the flow pattern within the reactor were severe. Disturbances due to this effect could have significantly increased the convective transport rate in the region of growth.
Figure 6.2.1 Growth rate of LMOCVD ZnSe as a function of laser pulse energy at 20 and 40 Hz laser repetition rates.

Above a pulse energy of about 40 mJ (100 mJ/cm² in Figure 6.2.1), the LMOCVD growth rates appear to reach maximum values of about 2.7 μm/h and 4.6 μm/h respectively for 20 Hz and 40 Hz operation. This behavior was an indication that significant depletion of the metalorganic species occurred in the region of the laser pulse. Further increases in laser pulse energy could not add to the growth rate, as only insignificant additional source material could enter the growth region during the 20 ns duration of the laser pulse. The growth rate
trends and the fact that laser energy was observed to exit from the reactor indicate metalorganic density depletion occurred during the laser pulse.

A model was constructed to examine the change in metalorganic density and laser power during each laser pulse. The metalorganic density was a function of both position in the reactor and time, and decreased as the molecules were dissociated by 193 nm photons. The rate of change of the density $N(x,t)$ can be expressed as:

$$\frac{dN(x,t)}{dt} = -\frac{\sigma N(x,t)I(x,t)}{\hbar \omega} \quad (6.2.1)$$

where $\sigma$ is the absorption cross-section of the metalorganic molecules at 193 nm ($\sim 2 \times 10^{-17}$ cm$^2$), $\hbar \omega$ is the photon energy (J), and $I(x,t)$ is the laser power density in J cm$^{-2}$ s$^{-1}$. The laser power density also changed with time and position in the reactor due to two effects. Energy was lost to absorption by the DESe and DMZ, but the slight focusing of the beam through the reactor increased the power density somewhat to counteract absorption. The decrease in power density due to absorption can be represented by the equation:

$$\frac{dI(x,t)}{dx} = -\sigma N(x,t)I(x,t) \quad (6.2.2)$$

The change in beam cross-section with position was estimated by assuming a linear change in area. The measured beam cross-section was 1.5 cm by 0.4 cm at the inlet to the reactor and 1.2 cm by 0.35 cm at the center after crossing 4.5 cm inside the reactor.

The equations for $I(x,t)$ and $N(x,t)$ were solved simultaneously using a numerical model with boundary conditions

$$N(x,0) = N_0 \quad (6.2.3)$$
\[ I(0,t) = I_0 \quad 0 \leq t \leq 18 \text{ ns} \]  \hspace{1cm} (6.2.4)

The algorithm used for the numerical simulation is presented in Appendix E.

The source gas density and laser power profiles calculated using a metalorganic density of $3.5 \times 10^{16} \text{ cm}^{-3}$ are shown below. The calculated profiles for metalorganic density and laser power density across the reactor at a time near the end of the laser pulse are shown in Figure 6.2.2 and Figure 6.2.3, respectively.

![Figure 6.2.2](image)

Figure 6.2.2 The calculated profiles for metalorganic density across the reactor near the end of the laser pulse.
Figure 6.2.3 The calculated profiles for laser power density across the reactor near the end of the laser pulse.

The source density is reduced by approximately 85% at the center of the reactor when a pulse energy of roughly 40 mJ is used and by about 95% for a 50 mJ pulse, which is consistent with the observed saturation of the growth rate (see figure 6.2.1). The power density of the laser pulse exiting the reactor is calculated to be significant for all pulse energies except 15 mJ, an observation also made during the experiment. Therefore, the metalorganic density in the reactor is probably very close to the value that was calculated using the bubbler transport equations. (See section 4.3) Matching calculated laser intensity
profiles to the observed saturation of the growth rate may be a good method to determine the actual metalorganic density.

The morphology, observed using Nomarski contrast microscopy, was very similar for all films grown in these experiments. The photomicrographs in Figure 6.2.4 are of films grown under the two extremes of film growth, 50 mJ pulse energy at 40 Hz (a) and 15 mJ pulse energy at 20 Hz (b). There was some surface texture on both films, though the film grown at the faster rate appeared to have a much rougher surface. Inclusions and surface debris were evident in these and all other films grown in this study, and were found on the thermally grown film as well. The debris may be incorporated in the film sometime during the beginning of growth since it was usually grown over or around in the thickest regions of the deposits. The origin of the debris is unknown, but it could arise from material from previous growth runs flaking off the reactor wall.

The optical properties of the epitaxial films in the laser power/pulse rate study were examined using photoluminescence (PL). A strong ionized-donor-bound exciton or acceptor-bound exciton emission was present at 2.793 eV ±0.002 eV in the PL spectra for most films with the exception of the thermally grown film. The MOCVD grown film was only 0.14 μm thick and luminesced very weakly. The films grown using a 20 Hz repetition rate were of better quality than those grown at 40 Hz. (see Figures 6.2.5 and 6.2.6) It is possible that the rate was too high at 40 Hz to get adequate surface movement to the desired lattice sites. The relative intensity of the self-activated emission near 2 eV compared to the bound exciton emission was highest for those films grown at 40 Hz, indicating the presence of a higher concentration of zinc vacancy-related
Figure 6.2.4. Photomicrographs of films grown at (a) 50 mJ pulse energy at 40 Hz and (b) 15 mJ pulse energy at 20 Hz. (scale = 100 μm)
Figure 6.2.5. The PL spectra of films grown at 20 Hz and four different pulse energies. a) 15 mJ, b) 28 mJ, c) 38 mJ, and d) 48 mJ.

complexes in the lattice. The PL spectra of the three thinnest films ($t < 1.0 \mu m$) were dominated by a donor-acceptor pair recombination band with no-phonon peak near 2.7 eV. Surface contamination would be more evident in the
Figure 6.2.6. The PL spectra of films grown at 40 Hz and four different pulse energies. a) 15 mJ, b) 28 mJ, c) 38 mJ, and d) 48 mJ.

Luminescence spectra of thin films than in thicker films. A donor-acceptor recombination band, P, which was observed by Dean with no-phonon line near 2.7 eV, may be associated with the presence of sodium acceptors. (52) These
three films were grown consecutively over three days, and it is possible that a contaminant such as sodium was introduced to the reactor during this time.

Selected films were examined using higher resolution PL at 1.6 K. Figure 6.2.7 contains the PL spectrum of a 1.3 μm thick film grown at 20 Hz with a 50 mJ pulse energy. The spectrum was taken over the high energy region from 4350 Å to 4850 Å with a resolution of 0.3 meV. The bound exciton transition was centered at 2.7950 eV with a full-width half-maximum of less than 4.5 meV. The relatively narrow line width was an indication that the material was single crystal, but also suggested strain in the material. Strain in ZnSe crystals causes a broadening of bound exciton lines to several meV and a shift to lower energy by 2 to 4 meV.(52) Photoluminescence at 2.7808 eV is most likely caused by the $I_1^{\text{Deep}}$ transition which has been associated with deep copper acceptors.(68) The presence of three LO phonon lines of the $I_1^{\text{Deep}}$ emission meant there was an extended lattice since phonon interactions of several orders were possible. The $I_1^{\text{Deep}}$ transition energy level was shifted down approximately 2 meV from the level measured by Dean (2.7830 eV), an indication of film strain.(68) The donor-bound exciton transition at 2.7950 eV was probably also shifted down in energy, and may be associated with the neutral donor-bound exciton emission associated with Ga, Cl or Al impurities. However, without the free exciton band emission to use as a reference, the assignment of the transition responsible for this emission cannot be made with certainty.

The high resolution PL spectrum of a 0.6 μm thick film grown at 20 Hz with a 15 mJ pulse energy is shown in Figure 6.2.8. A donor-acceptor recombination band with the no-phonon line centered at 2.694 eV dominated
Figure 6.2.7. The PL spectrum of a film grown at 20 Hz with a 50 mJ pulse energy taken over the high energy region from 4350 Å to 4850 Å with a resolution of 0.3 meV.
the spectrum, and several weak excitonic transitions were also present. The weak transition centered at 2.8016 eV was probably the free exciton emission because it was much broader than bound exciton transitions. The energy level of the free exciton emission was displaced to a lower energy by approximately 1 meV more than would be observed for strain free material. The other excitonic transitions were associated with neutral or ionized donors ($I_{2,3} = 2.7969$ eV), shallow acceptors such as Na or Li ($I_1 = 2.7925$ eV), and a deep acceptor ($I_{1\text{Deep}} = 2.7834$ eV).

Strong LO phonon coupling with both the donor-acceptor pair recombination and the deep acceptor transitions was found with energy spacings of approximately 31.5 meV. Again, the presence of the phonon lines was an indication of an extended lattice. Several distinct donor-acceptor recombination bands have been found in ZnSe luminescence spectra. (52, 66) The energy levels of the R, Q and P recombination bands vary strongly with excitation density and film thickness and strain. The presence of both deep and shallow (Li or Na) acceptor-bound exciton emissions make it difficult to assign a specific transition to the observed band. The energy level of the no-phonon line does, however, closely match the transition energy given by Dean and Merz for the Q band (Li).
Figure 6.2.8. The high resolution PL spectrum of the film grown at 20 Hz with a 15 mJ pulse energy.
6.3 Effect of Six Reactor Parameters on ZnSe Growth Rate

An experiment was designed to study the effect of reactor pressure, total flow rate, partial pressures of reactants, temperature and use of the laser on ZnSe film growth rate. The results from section 6.1 clearly indicated that ZnSe film growth and quality were strongly temperature dependent. The reactor conditions used in those experiments were chosen after examination of reported deposition conditions for ZnSe MOCVD in the literature and by trial and error experiments. The "best values" and relative importance of other reactor parameters such as pressure and flow rate were not known. A large number of sequential experiments would be required in order to completely describe the effect of these variables on film growth. However, useful information can be collected with many fewer experiments using a two-level multivariable experiment to identify the more important variables. (87)

Each variable of interest in a two-level multivariable experiment is investigated at two levels, a high and a low level, making a total of $2^n$ experiments required to study all possible combinations for $n$ variables. When all combinations of the variables are tested, the experiment is called a complete factorial experiment of order $n$. One half, or $2^{n/2}$, of the experiments are performed with a variable at its high value, while the other $2^{n/2}$ experiments are performed with the variable at its low value. For each of the growth characteristics of interest (e.g. growth rate) the average of the $2^{n/2}$ values obtained with the variable at its high value is compared with the average of the $2^{n/2}$ values obtained with the variable at its low value. The difference between the average of the results at the high and low levels is then compared to the
variance in the data to determine if the effect is statistically significant. In this manner, the effect of all \( n \) variables can be estimated from the results of a complete factorial experiment. Interactions between variables can also be examined.

For any six-variable set a total of 64 experiments would be required to run a complete factorial experiment. But, if it is assumed that all three-variable interactions and higher are unimportant, useful information can be obtained with a subset of the test conditions required for a complete factorial design. A 16 trial experiment is sufficient to gather information on all first order effects of the variables, with two-variable interaction effects confounded with one another, and greatly reducing the number of experiments needed.

A formalism exists for the design of such a set of experiments. The experimental design for factorial experiments can be generated from Hadamard matrices.\(^{(87)}\) The 16 x 16 Hadamard matrix used to design the experiments reported in this section is given in Table 6.3.1. The interaction effects in the table, such as AB, actually represent -AB.

The order 16 matrix can be used, which allows a full factorial experiment on 4 of the variables and which will still give us much useful information. The variables substrate temperature, DMZ partial pressure, ratio of DESe to DMZ, and total system pressure were chosen as the four most valuable to explore. These are represented as A, B, C and D in the design matrix shown in Table 6.3.1. When one of the variables is at its high value, it is represented as a "+" in the table, and when it is at its low value it is shown as a "-". Interaction between variables is also represented by the sign in the matrix under the respective column. For example, -AB is positive when A and B have opposite signs and
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negative when A and B have similar signs.

In order to accommodate additional (e.g. more than four) independent variables into the study, one can replace columns where higher order interactions are normally placed (e.g. column 8, which would represent the effect of the product of AB and D) with one of the other independent variables. This is done under the assumption that the higher order interaction is expected to be small, and can thus be ignored. Therefore, columns 8 and 11 (which originally represented three-variable interactions ABD and ABC) were used to determine the conditions for total flow rate and the use of the laser.

The high and low levels used for each variable in this study are listed in Table 6.3.2. The laser was chosen to be either on at the standard condition or off so the effects of other parameters for both MOCVD and LMOCVD could be examined. The substrate temperature was set at 412 °C and 575 °C to ensure that some growth occurred for the thermal growth experiments even at the lower

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<th>Low</th>
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<td>B - PDMZ (torr)</td>
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temperature. The partial pressure of DMZ was set at levels higher and lower than the standard condition (0.05 torr and 0.2 torr) while the DESe partial pressure was controlled by changing the source ratio (DESe/DMZ) from 10 to 1. The upper and lower setpoints of the other parameters were determined by limitations of the experimental apparatus. The total flow rate was limited to a maximum of 2000 sccm by the range of the mass flow controllers. The lowest transport rate of DMZ was limited by the minimum bubbler temperature and the minimum controllable carrier gas flow rate. This limited the total pressure in the reactor to approximately 300 torr.

The 16 trials were done at the conditions specified in the Hadamard matrix. (see Table 6.3.3) Growth times from 10 minutes to 80 minutes produced films with thicknesses from 0.2 μm to 2.2 μm. The calculated ZnSe growth rates were between 0.2 μm/h and 12.7 μm/h. The substrate was positioned underneath the heater and laser radiation passed parallel to and below it. This new orientation was chosen to minimize the film defects caused by the incorporation of any particles formed by gas phase nucleation, using gravity to separate them from the growth surface.

The growth rate results from the sixteen experiments were entered into the Hadamard matrix with the appropriate sign. (Table 6.3.4) The average difference between the rate of films grown at high and low levels for each reactor parameter or interaction was then determined by summing the values in the respective column and dividing by 8, the number of comparisons. The random error was estimated using the average difference calculated for the three-term interactions in columns 12 and 14, assuming that all three-variable
Table 6.3.3 Hadamard Matrix Experiment Reactor Parameters

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interactions are negligible. This random error was multiplied by a statistical correction factor (to account for the sample size used to determine the error) to define what average difference is statistically greater than would be expected for random error.
A sample variance of 0.84 μm/h was calculated for the growth rate using the three variable contrasts in columns 12 and 14; the average difference between high and low levels in these contrasts was a result of random error. The average difference between the high and low levels, Σ(\(X_H - X_L\))/8, in each contrast column was calculated (shown at the bottom of Table 6.3.4). This average was then compared to a test criterion for 90% confidence with two degrees of freedom (the degrees of freedom, Φ, is the number of data sets used to calculate variance) to determine if the observed effects could be statistically associated with the change in level of the variable. The results of these calculations are given in Table 6.3.4. From the calculations it was found that the effect of the variables or their interactions were significant if the average difference were greater than 0.8.

As expected, the ZnSe growth rate increased significantly with temperature, DMZ partial pressure, and DESe/DMZ ratio over the ranges used, and with the use of the laser. The total flow rate did not have a statistical effect on growth rate. An increase in pressure from 100 torr to 300 torr resulted in an average decrease in growth rate. At first glance this result may seem contrary to expected behavior. However, it must be remembered that the effect of total pressure is separated from the effect from changes in the reactant partial pressures. The decrease in growth rate with increasing pressure may be a result of worsening free convection in the reactor with increasing total pressure. (see equation 4.4.3) Three sets of confounded variable interactions were found to influence growth rate (columns 5, 9, and 15). The two-variable interactions temperature - DMZ partial pressure, total pressure - flow rate, and DESe/DMZ ratio - laser (column 5 in Hadamard matrix), temperature - DESe/DMZ ratio and
Table 6.3.4 Hadamard Matrix Test Criterion Values

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Σ \( 50.26 \) 32.36 23.84 12.78 -11.9 -23.2 -1.56 4.14 -0.3 -12.9 -0.96 16.26 0.12 0.7 -3.36 11.76

\|Σ/N\| 6.28 4.05 2.98 1.60 1.49 2.90 0.20 0.52 0.04 1.62 0.12 2.03 0.02 0.09 0.42 1.47
DMZ partial pressure - laser (column 9), and temperature - total pressure or DMZ partial pressure - flow rate (column 15) may significantly effect film growth rate. The possible significance of the temperature-total pressure interaction indicates there may be a similar reduction of the apparent activation energy with increasing reactor pressure as observed by Giapis et al. (35) No statement can be made concerning the influence of the other two-variable interactions on film growth because opposite effects can cancel out in the confounded contrasts.

The film quality of films grown during the matrix study were examined. The film morphology of the grown films were of two types, Figure 6.3.1. The films grown at 412 °C typically had a relatively smooth surface, with some texture as seen in Figure 6.3.1a, with debris clearly evident on top and in the film. Pits were observed, Figure 6.3.1b, in the surfaces of films grown thermally at 575 °C. Although the thermal process is expected to dominate the growth process at this temperature, the LMOCVD films exhibited both types of morphology.

There was much variability from sample to sample in the low resolution photoluminescence spectra and some spot to spot variability on individual films. Photoluminescence spectra for selected films grown at 412 °C and 575 °C are shown in Figures 6.3.2 and 6.3.3 respectively. The energy scale for these spectra is presented as the wavelength of the observed emissions, so the high energy end of the spectra is at lower wavelength. The PL spectra for eleven out of the sixteen films were dominated by strong emission from deep levels giving rise to broad peaks over the range from 5000 A to 6200 A. Emission from several different deep bands were evident in the spectra from other samples, with the self-activated center near 6100 A and another band centered
Figure 6.3.1. Morphologies of films grown in matrix study: (a) smooth, 412 °C LMOCVD and (b) pits, 575 °C thermal growth. (scale = 100 µm)
Figure 6.3.2. Low resolution photoluminescence spectra of selected films grown at 412 °C for the design of experiments matrix.
Figure 6.3.3. Low resolution photoluminescence spectra of selected films grown at 575 °C for the design of experiments matrix.
somewhere in the spectral range from 5300 Å to 5600 Å. These higher energy bands were not observed for films grown under near standard conditions and their presence was more prominent in films grown with a 1 to 1 source gas ratio. The broad emissions centered near 5400 Å could be associated with substitutional defects on the Se sites of the lattice, and would therefore be less likely to occur when the growth was done under an excess of the selenium source.

The best quality film was sample 14 which was grown at near standard conditions. The photoluminescence spectrum for this film had the strongest donor bound-exciton emission relative to deep level emission of any of the films from the Hadamard trial. This film also exhibited the best electrical characteristics. The room temperature resistivity was 0.325 Ω-cm with a free carrier density of 6.7 x 10^{16} cm^{-3} and mobility of 310 cm²/Vs. At 77 K the resistivity increased to 0.678 Ω-cm with a carrier density of 2.27 x 10^{16} cm^{-3} and mobility of 406. According to Ruda's theoretical calculations (72), these values correspond to carrier compensation ratios of greater than 0.96 and 0.94 at 300 K and 77 K respectively. The majority of the films were too resistive to make electrical measurements with the low impedance measuring system that was used.

6.4 Effect of Laser Incidence on LMOCVD ZnSe Growth

The majority of the experiments reported in this thesis were done with excimer laser radiation passing above and parallel to the substrate. Several growths, however, were performed with the laser beam incident to the surface at a shallow angle of between 20° and 30°. The laser beam entered the reactor
through the side MgF$_2$ window as in the parallel irradiation experiments. The heater support rod was rotated to position the substrate into the path of the laser beam. The heater was rotated just enough to ensure that the entire laser beam hit the substrate with minimal changes to the gas flow near the growth region. Three films were grown under identical flow conditions but with different laser parameters. The reactor was operated under the standard flow conditions (see section 5.2) with a substrate temperature of 400 °C. The source flow rates were decreased to one-half the standard values (1.2 sccm DMZ, 12 sccm DESe) because the growth rate was expected to increase significantly under perpendicular irradiation. Growth time was kept constant at 30 minutes.

Films were grown using 1) an unfocused laser beam with 20 mJ pulse energy at 40 Hz, 2) a focused beam with 20 mJ pulse energy at 40 Hz, and 3) a focused beam with 50 mJ pulse energy at 20 Hz. In the absence of gas phase absorption the laser energy densities for these three experiments would have been approximately 5 mJ/cm$^2$, 60 mJ/cm$^2$ and 140 mJ/cm$^2$, respectively. Although the damage threshold for GaAs is approximately 35 mJ/cm$^2$ with ArF excimer laser radiation, none of the films here exhibited any ablative damage. Therefore the gas phase absorption may have significantly decreased the laser beam energy density before the beam reached the substrate surface.

Films grown with the three different laser conditions, shown in the Nomarski photomicrographs in Figures 6.4.1 and 6.4.2, appear morphologically very similar overall to those observed on films grown under parallel laser irradiation. The two photographs in Figure 6.4.1 show film morphology a) near the center of the irradiated region for the film grown at lowest laser energy and b) a similar area grown under the highest laser energy density. Hillocks were
Figure 6.4.1. Nomarski photomicrographs of ZnSe films at the center of irradiated area, grown at the (a)lowest and (b)highest laser energies. (scale = 100 µm)
not present for either film like they were for films grown with parallel irradiation, although the general appearance was rougher. The ZnSe film grew around particles on the substrate surface in Figure 6.4.1a, with interference patterns in the laser radiation apparently affecting growth on the side of the particles away from the laser beam. These particles were totally covered in the thicker film grown at higher laser energy density. All three films showed the most morphological roughness at the near edge of the irradiated spot where the laser energy density was highest. Figure 6.4.2 is a photograph of the edge of this region on the film grown with a focused laser beam and 40 mJ pulse energy.

Figure 6.4.2. Nomarski photomicrograph of a ZnSe film near the edge of the area irradiated by a focused 40 mJ ArF pulse. (scale = 100 μm)
The rapid change in film thickness was evident by the closely spaced interference fringes. An area with very smooth surface morphology was observed on the film grown with the highest laser energy density near the edge of the grown film on the laser input side. One possible explanation for this difference in film appearance could be the increased heating of the area at higher incident laser pulse energy. Transient heating during each pulse might anneal the film in this region as it grew. Further experiments are needed to study this behavior.

The low resolution photoluminescence spectrum from the film grown using the unfocused laser beam is shown in Figure 6.4.3. The intensity from the donor bound-exciton emission, Figure 6.4.3, was the highest observed for any of the MOCVD or LMOCVD grown films reported in this thesis. The relatively weak self-activated emission compared to the bound-exciton emission was an indication of good film quality. The high resolution PL spectrum in Figure 6.4.4 contains a weak exciton emission at 2.7994 eV, strong donor bound-exciton emission at 2.7950 eV, deep acceptor bound-exciton emission at 2.7806 eV, and a weak donor-acceptor pair recombination band with no-phonon line at 2.6764 eV. Film strain appears to have shifted the transition energy levels down by 3.3 meV from the levels observed by Dean in MOCVD grown ZnSe. (see Table 3.3.2) (66) The film thickness was 0.84 μm in the thickest region, and film strain is expected to exist in ZnSe/GaAs films with thicknesses less than 1 μm(see Section 2.3). Therefore the exciton related peak at 2.7994 eV is possibly the free exciton emission and the intense emission at 2.7950 eV was most likely from a neutral Ga or Al donor-bound exciton.
The electrical properties of the same film were measured using the van der Pauw Hall method. The film resistivity was 3.85 $\Omega$-cm at 300 K with a free carrier density of $1.14 \times 10^{16}$ cm$^{-3}$ and mobility of 142 cm$^2$/Vs. At 77 K the

Figure 6.4.3. Low resolution photoluminescence spectrum from film grown using unfocused laser beam incident on the substrate.
resistivity decreased to 3.52 $\Omega$-cm with a free carrier density of $4 \times 10^{15}$ cm$^{-3}$ and mobility of 441 cm$^2$/Vs. This was the highest mobility measured for any film analyzed. The high mobility correlated well with the presence of a strong donor.

![Graph showing D-A Recombination and energy levels.](image)

**Figure 6.4.4.** High resolution photoluminescence spectrum from film grown using unfocused laser beam incident on the substrate.
bound-exciton emission and a weak self-activated band in the photoluminescence spectrum. The theoretical mobility of n-type ZnSe with carrier concentration on the order of $10^{15}$ is approximately $10^4 \text{ cm}^2/\text{Vs}$ at 77 K.\(^{(72)}\) The total ionized defect density corresponding to the measured free carrier concentrations and mobilities are approximately $5 \times 10^{18} \text{ cm}^{-3}$ and $7 \times 10^{17} \text{ cm}^{-3}$ respectively at 300 K and 77 K. Therefore the donor impurities are highly compensated by acceptor impurities or traps, with a compensation ratio near 1. The electrical properties for this film are very poor compared to those required for use in any device, but they are better than those measured for the majority of the films grown under other conditions in this study.

6.5 Quadrupole Mass Spectrometry of Zinc Selenide MOCVD

Gaseous products from the ZnSe MOCVD reactor were analyzed in situ using a quadrupole mass spectrometer. The sampling from high pressures such as 100 torr into the mass analyzer head was accomplished using a novel pressure reduction sampling inlet system. Jet separator and capillary sampling techniques that have been used for MOCVD sampling systems have tended to fill with particulates and condensate from the MOCVD reaction. A membrane sampling inlet system is less susceptible to particulate matter due to its relatively large transport area compared to a capillary inlet or orifice. Dimethylsilicone rubber has a high permeability to large organic molecules compared to that for hydrogen or helium carrier gases. Thus selective sampling of molecules and their by-products can be achieved using a dimethylsilicone membrane sampling system. The permeability of dimethylzinc (DMZ) is on the order of $10^{-3} \text{ cm}^2/\text{s} \cdot \text{cmHg}^{-1}$ compared to $6.5 \times 10^{-5} \text{ cm}^2/\text{s} \cdot \text{cmHg}^{-1}$ for
hydrogen. This technique has been used successfully to study DMZ concentration under changing conditions in an atmospheric pressure ZnSe MOCVD reactor. Operation of the membrane separator at room temperature gave sufficient separating power to detect DMZ with good resolution.

The reaction products from the ZnSe MOCVD reactor were monitored downstream using a VG Instruments 200D mass spectrometer with dimethylsilicone membrane inlet system. The gas stream was diverted from its normal path at a tee near the outlet from the reactor into the mass spectrometer sampling system and re-introduced into the MOCVD vacuum system at the inlet to the pyrolysis furnace. The membrane inlet was kept at a constant temperature of 30 °C inside a furnace to eliminate changes in permeability due to room temperature fluctuations.

Figure 6.5.1 is a mass spectrum of the by-products detected using the membrane inlet system during a ZnSe LMOCVD deposition. The reactor system was operated at the standard conditions for flow rates and pressures as specified in section 5.1. The substrate temperature was kept at 425 °C and the laser was operated at 40 Hz with 50 mJ pulse energy entering the reactor. A Faraday cup detector with lower limit on the sensitivity of 10^{-9} mbar was used to collect the data since the total pressure in the analyzer head exceeded 10^{-6} mbar during sampling. The majority of the detected mass peaks were from mass fragments of DESe and organic by-products. DMZ was detected at a much lower partial pressure in the analyzer head at mass to charge ratios (m/e) of 64, 66 and 68 (Zn+ isotopes). The remainder of the expected DMZ mass fragment peaks at 79, 81 and 83 amu (ZnCH_{3}^+) and at 94, 96 and 98 amu
(Zn(CH₃)₂⁺) were lost under the mass peaks from the more strongly detected DESe.

DESe mass peaks were detected in five groupings over the mass range from 76 to 140 amu. The highest detected partial pressure was just over 10⁻⁶ mbar for ethyl radicals at 27 and 29 amu. The permeability of DESe

![Graph of mass spectrum](image)

Figure 6.5.1. Mass spectrum of the by-products detected during a ZnSe LMOCVD deposition.

through the membrane appeared to be much greater than that for DMZ because the detected peak ratios for the two molecules was much greater than would be expected from the difference in partial pressures. The relative natural abundance of the six major isotopes of selenium are listed in Table 6.5.1. The mass peaks corresponding to the most abundant isotope (80 amu) were
detected at 80, 82, 95, 110, 123 and 138 amu. The mass fragments near 138 amu and 123 amu were present in the correct isotopic ratios for Se(C₂H₅)₂⁺ and Se(C₂H₅)(CH₂)⁺ respectively. The excess hydrogen in the analyzer head reacted with the lower mass fragments of DESe to form Se(C₂H₅)H⁺, Se(CH₂)H⁺, and SeH₂ (found at 110, 95 and 82 amu). Hydrogen selenide was a likely by-product of the MOCVD reaction. However the relative intensities of the 82 amu to 138 amu peak were nearly the same as the expected ratio for 80 to 138 without the presence of hydrogen, and therefore it was not possible to determine the presence of hydrogen selenide by-product.

DESe was allowed to flow through a cold reactor to monitor the transport rate and time evolution of DESe partial pressure in the reactor. A similar experiment was done with DMZ. The transport rates and conditions were identical to those used during experiments reported in section 6.1 and 6.3. The DESe was kept at 55.0 °C to obtain a vapor pressure of 109.4 torr.
Approximately 150 sccm of hydrogen carrier gas was flowed through the atmospheric pressure bubbler to reach a calculated DESe flow rate of 25 sccm. The tubing between the outlet of the bubbler and the bubbler throttle valve was heated to prevent condensation of DESe on the tube walls. A -2.5 °C bubbler temperature ($P_{DMZ} = 108.4$ torr) and 15 sccm carrier gas flow rate was used to reach a calculated DMZ flow rate of approximately 2.5 sccm. The hydrogen flow rate was adjusted to reach a 2000 sccm total flow rate. Several of the mass fragment peaks were monitored with time after the bubbler valves were opened.

The time evolution of the 79 amu DMZ signal and 110 amu DESe signal are shown in Figure 6.5.2. The DESe pressure reached a steady state after about 8 or 9 minutes from the time the bubbler was opened. The DMZ pressure, however, did not reach a steady state even after an hour of operation. With the flow rates that were used for these measurements the delay times before metalorganics should have reached the reactor were approximately 45 seconds for DMZ and 5 seconds for DESe. The average residence time between the inlet to the reactor and the mass spectrometer was less than 20 seconds. These delay times do not account for the large rise time of the species. Loss of metalorganics by some mechanism such as condensation on the walls or reaction with residual water vapor may have occurred.
Figure 6.5.2. Time evolution of the 79 amu DMZ and 110 amu DESe signals
Chapter 7
Conclusions and Recommendations

A reactor system has been designed and built for the laser-assisted metalorganic chemical vapor deposition (LMOCVD) of zinc selenide epitaxial films. Details of the source gas transport system, LMOCVD reactor, exhaust and exhaust treatment, and the electronic control system for valve sequencing and safety interlocking have been presented in Chapter 4. The basic parameters of operation for the LMOCVD system have been detailed.

The LMOCVD growth of ZnSe was achieved using 193 nm ArF excimer laser radiation to photodissociate the source gases dimethylzinc and diethylselenide. Film growth rate and quality were examined for a variety of reactor conditions, with a set of "standard conditions" used as a reference. (see section 5.2) Under standard flow conditions LMOCVD ZnSe was deposited at a nearly constant growth rate of about 1 \( \mu \text{m/h} \) over the temperature range from 200 °C to 400 °C, temperatures at which no thermal growth occurred. Use of the excimer laser radiation increased the film growth rate by nearly 1 \( \mu \text{m/h} \) over the thermal rate at higher temperatures, but the enhancement margin decreased with increasing temperature and at 550 °C the growth rates were approximately the same. Photoluminescence analyses of the films indicated that the best quality films were grown at the lower growth rate at 400 °C. Films grown at higher temperatures contained more dislocations and exhibited stronger emission from the defect-related self-activated center relative to donor-bound-
exciton emission. Film quality was poorest for the films grown below 400 °C, which had only very weak luminescence intensity and no excitonic emissions.

An increase in either laser energy density or laser repetition rate resulted in an increase in LMOCVD growth rate. The growth rate at 20 Hz increased from 1.1 µm/h at 15 mJ per pulse laser energy to 2.4 µm/h with a 48 mJ pulse energy and all other reactor conditions kept constant. The rate was approximately doubled when the laser repetition rate was increased from 20 Hz to 40 Hz. A leveling off of the growth rate at high pulse energies for 20 Hz operation indicated a possibility that the absorbing species in the laser beam path are bleached at pulse energy densities greater than about 100 mJ/cm². More experiments are required to examine this process in more detail.

A two-level Hadamard matrix experiment was done to examine the effect of six reactor parameters on film growth rate. Substrate temperature, DMZ partial pressure, DESe/DMZ source ratio, reactor pressure, and the use of the laser were all found to significantly affect the growth rate while the total flow rate did not. The change in flow rate in the study was too small to significantly affect the transport in the reactor which was dominated by natural convection. The photoluminescence analysis indicated that the highest quality film was grown under similar conditions to the standard used for other experiments. However, further experiments are required to determine the best values of DMZ partial pressure, DESe/DMZ ratio, and pressure to use in LMOCVD ZnSe growth.

The epilayers from both MOCVD and LMOCVD growth had generally smooth morphology, although some films grown at higher temperatures exhibited hillock formation. All films had ZnSe particles embedded into the film or littered on top, which could have been the result of gas phase nucleation.
A small number of experiments were done with the laser radiation incident on the growth surface. One of these films, grown at a laser energy density less than approximately 5 mJ/cm², exhibited both the highest carrier mobility and one of the highest donor bound-exciton to self-activated center luminescence ratios. Although further experimentation is necessary to investigate the effect of surface irradiation during LMOCVD, this may indicate that a surface interaction is required to obtain the best films. One particularly interesting experiment would be to use 248 nm KrF excimer laser radiation as the excitation source where the growth process would be dominated by surface interactions. The gas phase species are nearly transparent to 248 nm radiation while adsorbed species are not because of the red shift in their absorption spectra. As long as the laser energy density is low enough to eliminate any two-photon dissociation of metalorganic sources, surface reactions will drive the growth process.

Natural convection effects dominated the flow patterns in the current reactor. Since laminar flow conditions are desirable to minimize gas phase reactions which are harmful to good epitaxial growth, an inverted flow horizontal reactor, with the substrate located on the upper wall of the reactor, was designed. This design overcomes natural convection by ensuring that the hottest region of the reactor is at the top. The reactor was built and is now in use. This configuration will minimize the chance of gas phase nucleation by preventing vortex formation and also prevent the incorporation of gas phase particulates into the film since gravity will help to separate them from the surface.
Better temperature measurement techniques are needed. In the inverted flow reactor the substrate will be placed on a resistively heated susceptor, and thermocouples embedded in the heated block should allow reliable temperature control. Infrared pyrometry might result in even more accurate temperature measurement.

The product stream from the LMO CVD reactor has been analyzed using a membrane inlet to sample at high pressures with selectivity to the metalorganic species over the hydrogen carrier gas. The transient rise time for the concentrations of the metalorganic species after bubbler transport began was longer than expected, possibly a result of condensation or reaction on the reactor or tubing walls. To overcome this problem, a load lock could be installed on the reactor. Currently the reactor is opened to atmosphere for a minimum of several minutes for the exchange of substrates, and during this time air and water could be adsorbed on the walls. Use of a load lock would minimize the amount of air that entered the reactor. Another design change that may be beneficial would be to change to a run/vent switching manifold. This system would have a "vent" line in parallel with the reactor, and a switching manifold at the reactor inlet that directs two gas streams of equal flow rate into either the reactor or the vent. The vent line would be constructed to achieve equal pressure drops across the reactor and the vent. Prior to a growth run the metalorganic transport is begun through the vent. After the metalorganic transport is at steady state the manifold would be switched to start flow of source gases into the reactor.

The important parameters for ZnSe LMO CVD have been identified and detailed over a limited range of temperature and laser parameters. Low growth
rates at 400 °C have yielded the best results so far for parallel irradiation, and there is an indication that incident radiation could have a positive effect on film quality. However, all material is heavily doped due to difficulties with impurity control. The diethylselenide source, nominally electronic grade, is of low purity (99.995%) for electronic applications. An improvement in metalorganic source quality is essential for the growth of useful material by LMOCVD.
References


### Appendix A
### Equipment List

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
</table>
| APB          | Absolute Pressure Baratron, MKS Instruments Inc.  
model 222CA-01000BB, 0 to 1000 torr  
model 222BA-01000B, 0 to 1000 torr  
model 221AA-01000B, 0 to 1000 torr |
| Blower 1     | Direct Drive Blower, Dayton  
model 4C685 |
| Blower 2     | Shaded Pole Blower, Dayton  
model 4C054 |
| CGM 1        | Combustible Gas Monitor, Sierra Monitor Corp.  
model 2001, alarm level 300 ppm H₂ |
| CGM 2        | Lauda Constant Temperature Bath,  
Brinkmann Instruments, Inc.  
model RMT-6, -15°C to 100°C, 0.1°C accuracy |
| CV 1         | Control Valve, MKS Instruments, Inc.  
model 248A-00500RV  
500 sccm maximum flowrate |
| CV 2         | model 248A-02000RV,  
2,000 sccm maximum flow |
| CV 3         | model 248A-10000RV,  
10,000 sccm maximum flow |
| Fil 1        | Particle Filter, Balston, Inc.,  
Microfibre, 0.1 mm, Grade AQ |
| Fil 2        | Particle Filter, Balston, Inc.,  
Microfibre filter tube model 100-25-DH  
Stainless steel filter housing model 4556 |
| Furnace      | Pyrolysis Furnace,  
model unknown |
| HP           | Hydrogen Purifier, Johnson Matthey, Inc.,  
model HP-50-VCR |
IPR  In-line Pressure Regulator, Linde Union Carbide, model SG3810-100

MFC  Mass Flow Controller, Unit Instruments, Inc.
MFC 1 model UFC-1000, 20 sccm Hz
MFC 2 model UFC-1000, 200 sccm Hz
MFC 3 model UFC-1000HP, 200 sccm Hz
MFC 4 model UFC-1000HP, 1000 sccm Hz
MFC 5 model UFC-1000HP, 1000 sccm Hz
MFC 6 model UFC-1000HP, 20 sccm Hz
MFC 7 model UFC-1000HP, 200 sccm Hz
MFC 8 model UFC-1000, 200 sccm Hz
MFC 9 model UFC-1000, 200 sccm Hz

OFS  Oil Filtration System, Leybold-Heraeus Vacuum Products, Inc. model OF-1000, activated alumina filter element

ORP  Oxygen Removing Purifier, Johnson Matthey, Inc. model OR-50

PC 1 Pressure Controller, MKS Instruments, Inc.
PC 2 model 250 B-1-D
PC 3

PT  Pressure Transducer, Omega Engineering, Inc. model PX 236-100 GV, 0-100 psig

Pump  Rotary Vane Pump, Leybold - Heraeus Vacuum Products, Inc. model D30AC, 26.8 CFM displacement

SV  Solenoid Valves, Peter Paul Electronics model 053 Z 00321 GB, 12 VDC

TC 1 Thermocouple, Substrate, Omega Engineering, Inc. model SICSS-032U-18

TC 2 Thermocouple, Furnace, Omega Engineering, Inc. model TJ36-CAIN - 18U-12

TCon 1 Temperature Controller, Substrate, Omega Engineering, Inc. model CN310-J-C

TCon 2 Temperature Controller, Furnace, Omega Engineering, Inc. model CN5001 K2 - FI-EG
<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trap</td>
<td>Pump Inlet Absorption Trap, Leybold-Heraeus Vacuum Products model 85416 basket-type trap activated alumina beads in lower layer KOH impregnated charcoal in top layer (charcoal from Contamination Control, Inc.)</td>
</tr>
<tr>
<td>Valve 1</td>
<td>Air Operated Bellows Valve, Upstream of Reactor, Nupro Co. model SS-BNVCR4-C</td>
</tr>
<tr>
<td>Valve 2</td>
<td>Air Operated Bellows Valve, Downstream of Reactor, Nupro model SS-BBK-VCR-1C</td>
</tr>
<tr>
<td>WRP</td>
<td>Water Removing Purifier, Matheson Gas Products model 450 housing model 452 cartridge</td>
</tr>
</tbody>
</table>
Appendix B
System Controller Electronics

There were a total of 35 valves for gas switching in the MOCVD reactor system. A set of push button controls was designed for valve sequencing during typical growth procedures. Fifteen different modes, or valve configurations, could be chosen from the push button control panel. The first mode selected valve operation through a manual control panel with toggle switches to operate each valve individually. The remaining fourteen valve configurations were programmable using sets of DIP switches in the controller electronics. As a safety precaution, one mode was configured to have all valves closed. This mode, mode 15, was used as an emergency shut-off and could be activated manually using the push button on the control panel or automatically by safety interlocks that monitored several inputs to avoid unsafe reactor conditions. The system was designed to power up into this failsafe mode.

Valve Controller

The heart of the valve controller is TTL circuitry that "latches" the system into a fixed state when an input from the control panel is received. The push buttons on the panel are wired into a TTL circuit to avoid voltage spikes or ringing that can occur with some switches and ensure a clean signal to the main controller electronics. (see Figure B.1) The circuitry used for the main controller is shown in Figure B.2 and B.3. Normally, the inputs to the LS273 latch is held high through a bank of 10 k\(\Omega\) resistors. When a button from the panel is selected, the corresponding input to the latch is pulled to ground. At the same
Figure B.1 Push button debouncing circuit.

The outputs from the latch control the state of fifteen banks of line drivers that are wired in parallel to each other. (Figure B.3) Each line driver has only eight inputs and outputs, so a bank of five line drivers is required to determine the state of all 35 valves. At the input to each bank of line drivers are manually programmable DIP switches. The outputs corresponding to control for each valve are wired together in parallel and turn on or off relays that control 12 volt solenoid valves. Each mode is programmed by grounding the input to the line drivers corresponding to the valves that need to be opened. The line drivers (74ALS746) are in a high impedance state, and act as an open circuit, if their input control voltage from the latch is high. Only the bank of five line drivers with grounded control voltage acts like a closed circuit. The line driver output
Figure B.2  Valve Controller Electronics - Mode Selector
voltages are inverted from the input voltages, so that if the input is grounded the line driver output is high.

The signals from the line drivers each pass through an inverter and determine the on or off state of high current relays. (Figure B.3) These relays supply twelve volts to 35 solenoids that control the air pressure supplied to the valves in the reactor system. A grounded input to the line driver gives a high output which is then inverted to ground one side of the relay. This turns the relay on, causing the solenoid valve to open and supply air to operate the desired valve. By programming several commonly used valve configurations into the valve controller modes, rapid and accurate valve switching was possible for the operation of the MOCVD system.
Safety Interlocks

Several safety interlocks are included in the controller electronics to avoid dangerous conditions in the laboratory. Reactor pressure, both bubbler pressures, the air supply pressure and two combustible gas detectors are all monitored. (see Figure B.4) These inputs are compared to safety levels using differential amplifiers. No problems are detected when the output from the amplifiers are all high. When one of the monitored inputs goes outside the safety limit, the output from the amplifier goes to ground. This causes the output from a series of AND gates to also go low and trigger a LS74 circuit, causing its Q output to go high. When this happens, several events take place almost simultaneously. The high output from the LS74 turns on a transistor by creating a positive base to emitter voltage drop. The transistor collector current turns on a relay that acts like a switch on the valve control panel, selecting mode 15 the failsafe condition and closing all valves in the reactor system. (see Figure B.2) The output from the LS74 also triggers a LS273 latch that will turn on LEDs indicating which safety interlock has failed. An interlock disable switch was placed in the circuit to bypass the relay so the reactor system could be operated to remedy an problems. After the fault is corrected, the system can be enabled by pushing a reset button that clears the LS74 circuit to give a low output which turns off the drive transistor and resets the latch.
Figure B.4 Safety Interlock Control Electronics
Appendix C
Gas Flow Calculations

Calculations were made to determine the relative importance of natural convection in the horizontal MOCVD reactor. The relative importance of buoyancy effects to inertial forces is determined by the dimensionless quantity Grashof number divided by the Reynold's number squared \( \text{GrRe}^{-2} \). (79) This quantity is calculated below. Two assumptions are made: i) gas properties are approximately those of hydrogen and ii) the system acts like an ideal gas.

The Grashof number and Reynold's number are defined by

\[
\text{Gr} = \frac{\rho^2 g \beta \Delta T D^3}{\mu^2} \quad \text{(C.1)}
\]

\[
\text{Re} = \frac{\rho \nu D}{\mu} \quad \text{(C.2)}
\]

where

\( \rho \) = gas density at the wall temperature (g cm\(^{-3}\))

\( g \) = acceleration due to gravity (980 cm s\(^{-2}\))

\( \beta \) = coefficient of volume expansion, ~ \( 1/T \) for an ideal gas (K\(^{-1}\))

\( \Delta T \) = temperature difference between heat source and chamber wall (K)

\( D \) = characteristic dimension, the tube diameter (8.255 cm)

\( \mu \) = gas viscosity (g cm\(^{-1}\) s\(^{-1}\))

\( \nu \) = average flow velocity (cm s\(^{-1}\))
Combining the equations and replacing $1/T$ for $\beta$ gives

$$\frac{Gr}{Re^2} = \frac{g \Delta T D}{T v^2}$$  \hspace{1cm} (C.3)

The variables must all be in terms of controllable parameters for us to directly calculate this quantity. The average velocity can be expressed as a function of the volumetric flow rate $Q$ and tube cross-sectional area $A$.

$$v = \frac{Q}{A} = \frac{4 Q}{\pi D^2}$$  \hspace{1cm} (C.4)

The actual flow rate measured with the mass flow controllers is in standard cubic centimeters per minute, $Q_0$. $Q$ is related to $Q_0$ for an ideal gas by

$$Q = Q_0 \frac{P_0 T}{T_0 P}$$  \hspace{1cm} (C.5)

where $T_0$ and $P_0$ are standard temperature and pressure (298K and 760 torr respectively). The quantity $Gr Re^{-2}$ in terms of controllable reactor parameters is

$$\frac{Gr}{Re^2} = \frac{\pi^2 g T_0^2 P_0^2 D^5 \Delta T}{16 P_0^2 Q_0^2 T^3}$$  \hspace{1cm} (C.6)

Under the typical conditions used during the current work

$P = 100$ torr

$Q_0 = 2000$ sccm = 33.33 sccs
Therefore

\[ \frac{Gr}{Re^2} = \frac{\pi^2 (980 \text{ cm}^2) (298 \text{ K})^2 (100 \text{ torr})^2 (8.255 \text{ cm})^5 \Delta T}{16 (760 \text{ torr})^2 (33.33 \text{ cm}^3 \text{s}^{-1})^2 T^3} \] (C.7)

The arithmetic mean, \( T_m \), can be used as an estimate of the average gas temperature. The actual value has to be something between the high temperature at the substrate and the cool wall temperature (which we assume to be 300 K). The value of \( Gr \ Re^{-2} \) at several temperatures over the range used during this study are listed in Table C.1. Under typical conditions the value was on the order of 100, meaning that free convection must dominate the gas flow.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( T_m ) (K)</th>
<th>( \Delta T ) (K)</th>
<th>( Gr \ Re^{-2} )</th>
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<tr>
<td>500</td>
<td>400</td>
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<td>900</td>
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Table C.1 Value of \( Gr \ Re^{-2} \) for Typical Film Growth Conditions
Appendix D
Hadamard Matrix Trial Calculations

The average effect of the six variables and their interactions on growth rate was determined by summing the measured growth rates using the signs in the corresponding column from the Hadamard matrix and then dividing by eight, the number of comparisons. (see Table D.3) Columns 12 and 14 represented three variable interaction effects and any difference was assumed to be due to random errors. The experiment variance $S_{\text{avg}}$ was estimated by averaging the variances $S_i$ from these two columns by

$$S_i^2 = \frac{(\Sigma X_{\text{high}} - \Sigma X_{\text{low}})^2}{8}$$  \hspace{1cm} (D.1)

$$S_{\text{avg}}^2 = \frac{S_{12}^2 + S_{14}^2}{2}$$  \hspace{1cm} (D.2)

to obtain $S_{\text{avg}}^2 = 0.706$ and $S = 0.84$ with two degrees of freedom. The effects from each column were then compared to the test criterion

$$|\bar{X}_{\text{high}} - \bar{X}_{\text{low}}| = t_\alpha S \sqrt{\frac{1}{N_{\text{high}}} + \frac{1}{N_{\text{low}}}}$$  \hspace{1cm} (D.3)

where $t_\alpha$ is the single-sided t-value for two degrees of freedom at the confidence limit required and $N_{\text{high}} = N_{\text{low}} = 8$. The $t_\alpha$ with a 10% chance of error is 1.89, making the test criterion value 0.79 The effects from the variables
and interactions of Table D.3 were significant if the average difference between
the high and low levels were greater than or equal to the test criterion
(represented as row $|\Sigma/N|$ in Table D.3).

The experimental design techniques used for this experiment are
discussed in reference 87.
Table D.1 Experimental Data from Hadamard Matrix Experiment

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Thickness (μm)</th>
<th>Growth Time (h)</th>
<th>Rate (μm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.93</td>
<td>0.33</td>
<td>2.82</td>
</tr>
<tr>
<td>2</td>
<td>1.58</td>
<td>0.25</td>
<td>6.32</td>
</tr>
<tr>
<td>3</td>
<td>2.17</td>
<td>0.17</td>
<td>12.77</td>
</tr>
<tr>
<td>4</td>
<td>2.22</td>
<td>0.25</td>
<td>8.88</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>0.92</td>
<td>0.30</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>0.33</td>
<td>0.76</td>
</tr>
<tr>
<td>7</td>
<td>1.14</td>
<td>0.53</td>
<td>2.15</td>
</tr>
<tr>
<td>8</td>
<td>1.54</td>
<td>0.33</td>
<td>4.67</td>
</tr>
<tr>
<td>9</td>
<td>0.89</td>
<td>0.20</td>
<td>4.45</td>
</tr>
<tr>
<td>10</td>
<td>0.16</td>
<td>1.00</td>
<td>0.16</td>
</tr>
<tr>
<td>11</td>
<td>0.93</td>
<td>0.52</td>
<td>1.80</td>
</tr>
<tr>
<td>12</td>
<td>0.18</td>
<td>0.28</td>
<td>0.64</td>
</tr>
<tr>
<td>13*</td>
<td>1.33</td>
<td>0.33</td>
<td>4.03</td>
</tr>
<tr>
<td>14*</td>
<td>1.09</td>
<td>0.25</td>
<td>4.36</td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>1.33</td>
<td>0.18</td>
</tr>
<tr>
<td>16</td>
<td>0.10</td>
<td>0.66</td>
<td>0.16</td>
</tr>
</tbody>
</table>

* experiments done at 40 Hz. Growth rate divided by two for analysis.
Appendix E

Laser Intensity and Metalorganic Density Algorithm

The following program was written to estimate the laser intensity and metalorganic species density in the reactor. The program was run in the program MatLab on a Macintosh II computer.

```c
%control.m

%An M-file to study bleaching
s=input('how many position points ?');
E=input(' pulse energy (in mJ) ?');
lo=(E*1e-3)/(1.8e-8);
inteno=lo*ones([1:s]);
for i =1:s
    inteno(i) = inteno(i)*(1.9+1.7*(i/s));
end

den=input('absorber density'); %on the order of 10e16
n=den*ones([1:s]);
delt=input('what time increment (nsec) do you want ?');
delt=delt*1e-9; %typical value is 1 nsec
steps=input('how many steps do you want ?'); %typically 20 nsec

for i = 1:steps
    inten = inteno;
    inten=decay(inten,n);
    n = bleach(inten,n,delt);
end
semilogy([inten;n])
pause
plot(n')
```
answ= input('save data ?', 's');
an=strcmp(y', answ);
if an == 1
    INT=[INT inten'];
    N = [N n'];
end

%decay.m
function y = decay (inten, n)
% decay calculates an iteration of the light decay
 m = length(inten);
deltax=7/m;
alpha=2e-17*n;
for i=1: m-1
    inten(i+1)=inten(i) - alpha(i)*inten(i)*deltax;
    if inten(i+1) < 1
        inten(i+1)=1;
    end
end
y = inten;

%bleach.m
function y = bleach(inten,n,delt)
%this function calculates the bleaching
%factor for the next time step
sigma=2e-17; %absorption cross section in cm-2
hu = 4.16e-19; %photon energy in joules
B=(sigma/hu)*n; %Einstein B coefficient as a function of position
m = length(inten);
for i = 1: m
    n(i) = n(i) - B(i)*inten(i)*delt;
        if n(i) < 1;
            n(i) = 1;
        end
    end
y=n;