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MOCVD growth of p-doped thin-film ZnSe

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MOCVD Growth of p-doped thin-film ZnSe

by

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MOCVD Growth of p-doped thin-film ZnSe

Apolak Borthakur

Abstract
Zinc Selenide (ZnSe) is a II-VI semiconductor with a band gap of 2.67 eV. The large bandgap makes it a promising material for the development of blue-green electro-optic devices and for the improvement of the storage density of memories. The major research problem associated with ZnSe is the difficulty in doping it p type. While there have been reports of good p doped ZnSe grown by molecular beam epitaxy (MBE), there have not been any reliable reports of heavily doped p type ZnSe grown by metal organic chemical vapor deposition (MOCVD). MOCVD is a much cheaper process than MBE. It has high throughput and can be used for commercial production. Thus it is of great interest to investigate the development of ZnSe by MOCVD. We report here a MOCVD technique for obtaining high quality p doped ZnSe. Growth parameters have been optimized to yield p type ZnSe doped to as much as $7.9 \times 10^{17}/\text{cm}^3$, which should be adequate for development of ZnSe blue-green LEDs.
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Chapter 1

Introduction

Zinc Selenide (ZnSe) is a II-VI compound semiconductor having a direct bandgap of 2.67 eV at room temperature. Recently it has been receiving a lot of attention as a promising material for development of electroptic devices in the blue-green region of the optical spectrum. ZnSe has a wide bandgap which makes it a promising material for blue LED fabrication. With the availability of a blue LED, manufacture of flat-screen displays would be easy, as LEDs of the other two primary colors, red and green, are already available. Then it would be possible to obtain flat-screen displays of high quality for use as color monitors for computers and televisions, for instance. Blue LEDs would also have a big impact on shrinking optical memory sizes, utilizing efficient optical memories. These devices scale as $1/\lambda^2$, so a large bandgap material would lead to large reductions in size. The strong non-linear properties of these polar materials can be used for unique optical devices as well [1,2]. Another use of ZnSe could be as an insulator to GaAs. One of the major drawbacks of GaAs as compared to Si is the fact that while it is very easy to obtain an effective insulator, SiO$_2$, on Si, no such insulator exists for GaAs. However, ZnSe has a very good lattice match with GaAs, and the interface state density is also extremely low. That makes it a
promising material for forming an insulating layer on GaAs, which might find use in GaAs MISFETs.

Device applications require material with very few defects and controllable properties. Such material can be obtained by epitaxial growth processes like molecular beam epitaxy (MBE) or metal organic chemical vapor deposition (MOCVD). Growth of high quality ZnSe by MBE has been demonstrated [3–6]. But, MBE is a very expensive process having extremely stringent vacuum requirements. It has a low throughput, and is not suitable for mass production. MOCVD, on the other hand, is a much cheaper process and has high throughput. Thus it is of practical interest to investigate the possibility of obtaining good quality ZnSe by MOCVD, and considerable effort is already underway in this area [7–14].

To fabricate a LED, we require both n and p doped ZnSe. It has been observed that most wide bandgap II-VI compounds take on one carrier type when prepared 'undoped', viz, when grown without introducing impurities of any kind. ZnSe ends up being n type when prepared undoped. It is easy to enhance the doping density of the natural carrier type, and ZnSe can be easily heavily n doped. MBE growth of n doped ZnSe has been demonstrated using chlorine [15, 16] or gallium [17, 18] as the dopant, and high carrier concentrations ($1 \times 10^{19}$/cm$^3$) and low resistivities ($3 \times 10^{-3}$ ohm-cm) have been attained. Iodine [19] or aluminum [20] have been used as dopants in MOCVD growth of n type ZnSe, and comparable carrier concentrations and resistivities have been obtained.
The major stumbling block in the effort to develop a ZnSe blue LED has been the difficulty in getting good p doped ZnSe. There have been theories proposed to account for this, [21–23], and it is generally believed that a process of self-compensation makes it difficult to obtain p type ZnSe. Self-compensation causes the formation of compensating donor-like defects to become energetically favorable after a certain density of acceptors has been incorporated into the lattice, bringing about a decrease in the net acceptor concentration.

There have been some reports of p type ZnSe grown by MBE [24–31]. Lithium has been examined as a dopant, but it has been found that the maximum carrier concentration obtainable is no more than $8 \times 10^{16}/\text{cm}^3$. Park, et al., have reported mid $10^{17}$ carrier concentrations in Nitrogen doped ZnSe, using NH$_3$ as a dopant. The highest carrier concentration reported so far has been $1 \times 10^{18}$ by a group from the 3M company [32]. They used a RF plasma source to obtain the dopant, N, from N$_2$. They have also demonstrated a preliminary blue-green laser diode emitting light at 490 nm [33]. The p doped ZnSe used in the diode had a carrier concentration of $3 \times 10^{17}/\text{cm}^3$.

There have been some reports of p doped ZnSe grown by MOCVD [34–36,12,37, 38], but most of them are unreliable, as contacts made of Au were used in performing Hall measurements. Later, it was found out that Au does not form an ohmic contact with p type ZnSe (ohmic contacts are necessary in the Hall method), but rather forms a Schottky barrier. Ohki, et al., [39] have claimed nitrogen incorporation of
as much as $10^{19}$/cm$^3$, using SIMS as the measuring technique, in their MOCVD-grown films. However, it has been shown by the 3M group [32] that the amount of electrically active nitrogen (which is indicated by C-V measurements) can be orders of magnitude less than the total nitrogen incorporated into the lattice (which is what SIMS indicates), and thus Ohki's result does not necessarily reflect the electrically active nitrogen content. The only paper that does present reliable C-V data on p doped ZnSe is by Taskar, et al., [40]. But, they have been able to obtain a maximum carrier concentration of $2 \times 10^{16}$/cm$^3$, which is about an order of magnitude less than what is needed for a useable ZnSe p-n diode.

In our work, we have been able to achieve up to $7 \times 10^{17}$/cm$^3$ electrically active p type carriers (nitrogen) using a custom built MOCVD reactor and NH$_3$ as the dopant. An annealing technique has been employed to electrically activate the carriers. The dependence of the carrier concentration on the annealing temperature has been examined. Also presented are data detailing the effect of changing the growth temperature and the ammonia flow rate on the carrier concentration. We have also investigated the effect of UV irradiation during growth, as well as the effect of using an ArF laser beam to photodissociate the precursors.

Chapter 2 provides a background on the theory of metal-semiconductor structures, photoluminescence and semiconductor characterization techniques. Chapter 3 provides a brief review of the equipment used. Chapter 4 describes the experiments
performed and the results obtained. Chapter 5 concludes with recommendations for future work.
Chapter 2

Background

2.1 P-n junctions

In this section we present a brief review of p-n junctions. Figure 2.1 depicts the electron energies at the edges of the conduction and valence bands for separated p and n type samples and also for p and n type samples in contact, forming a p-n junction. After contact, electrons diffuse from the n to the p side, holes diffusing the other way, setting up an equilibrium potential difference $V_{bi}$, called the built-in potential. The built-in potential appears across the depletion region (which extends from $x_{dp}$ on the p side to $x_{dn}$ on the n side), and $V_{bi} = V_{bip} + V_{bin}$. The depletion regions formed contain space charges due to the presence of individual, immobile doping ions. Using Gauss's law, we get

$$\frac{dE(x)}{dx} = \frac{\rho(x)}{(\epsilon_r \epsilon_0)}, \quad (2.1)$$

which relates the electric field $E(x)$ at the position $x$ to the space charge density $\rho(x)$ (equal to $eN_a(x)$ and $eN_d(x)$ in the p and n type materials respectively), where $\epsilon_r$ is the relative permittivity (dielectric constant) of the semiconductor and $\epsilon_0$ is the permittivity of free space. Using the definition of potential difference as the integral of
Figure 2.1: PN Junctions
E(x) with respect to x (Poisson's Equation), we can then get the relationship between
V_{bip} and V_{bin} and the respective depletion widths x_{dp} and x_{dn}.

For the case of uniform doping in both n and p regions, this leads to

$$x_{dp} = \left( \frac{2\varepsilon_r \varepsilon_0 V_{bip}}{eN_n} \right)^{0.5} \tag{2.2}$$

$$x_{dn} = \left( \frac{2\varepsilon_r \varepsilon_0 V_{bin}}{eN_d} \right)^{0.5}, \tag{2.3}$$

where N_n and N_d are the acceptor and donor dopings respectively of the two parts of
the p-n junction.

From the expressions (2.2) and (2.3) above, it can be seen that if, for example, the
n doping is very much larger than the p doping, then x_{dn} is much smaller than x_{dp}, the
effect is that almost all the depletion region and almost all of the built-in potential
occur on the p side. Thus, for a one-sided n^+-p junction (where n^+ indicates relatively
larger n doping), the relationship between the total built-in depletion thickness x_{dbi}
and the total built-in potential V_{bi} is given by

$$x_{dbi} = \left( \frac{2\varepsilon_r \varepsilon_0 V_{bi}}{eN_n} \right)^{0.5}. \tag{2.4}$$

If we evaporate a suitable metal on a p type semiconductor, we can in effect get a one-
sided diode, with the metal acting as the n^+ part. This a structure is called a Schottky
diode, and is used for C-V measurements to determine the carrier concentration of
the p type semiconductor. Let us turn our attention to Schottky structures.
2.2 Schottky Barriers

The work function $q\phi_m$ of a metal is the energy required to remove an electron at the Fermi level to the vacuum outside the metal. When negative charges, say, are brought near a metal surface, positive (image) charges are induced in the metal. When this induced image force is combined with an applied electric field, the effective work function is somewhat reduced. This lowering is called the Schottky effect, and we notice this effect in potential barriers arising in metal-semiconductor contacts.

If a metal with a work function $q\phi_m$ is brought in contact with a semiconductor that has a work function $q\phi_s$, charge transfer occurs until the Fermi levels line up in equilibrium. If, for instance, $\phi_m > \phi_s$, the semiconductor Fermi level is higher than that of the metal before contact. When the metal and the semiconductor are brought in contact, the Fermi levels have to line up. To achieve this, the electrostatic potential of the semiconductor must be raised (that is, the electron energies must be lowered) relative to that of the metal.

Consider an n type semiconductor, as in Figure 2.2. A depletion region $W$ is formed near the junction. The negative charge on the metal balances the positive charge due to uncompensated donor ions. The band bending is similar to what happens in a p-n junction. As seen in Figure 2.2, the bands have to bend by $q(\phi_m - \phi_s)$, and this is the built-in voltage $V_{bi}$. The barrier between the metal and the semiconductor now becomes $q(\phi_m - \chi)$. The depletion width $W$ can be calculated using the expression derived earlier for the $p^+\text{-}n$ diode.
Figure 2.2: Metal:n type semiconductor Schottky barrier

The case of a Schottky barrier on a p type semiconductor is illustrated in Figure 2.3. We get a Schottky barrier on a p type semiconductor when $\phi_m < \phi_s$. Aligning the Fermi levels at equilibrium requires a positive charge on the metal side and a negative charge on the semiconductor side of the junction. The depletion region now has negatively charged ionized acceptors, $N_a^-$. The potential barrier $V_o$ retarding hole diffusion from the semiconductor to the metal is $\phi_s - \phi_m$, and as before, this barrier can be lowered or raised by application of voltage across the junction. We have to keep in mind that the electrostatic potential barrier for positive charge is opposite to the barrier on the electron energy diagram.
The other types of ideal metal-semiconductor contacts ($\phi_m < \phi_s$ for n type semiconductors, and $\phi_m > \phi_s$ for p type semiconductors), result in non-rectifying or ohmic contacts. We will discuss these shortly.

2.3 I-V Characteristics of Schottky Diodes

When a forward-bias voltage $V$, is applied to a Schottky barrier, as in Figure 2.4, the contact potential is reduced from $V_o$ to $V_o - V$ (Figure 2.4). Electrons in the semiconductor conduction band can diffuse across the depletion region to the metal, giving rise to a forward current (metal to semiconductor) through the junction. On the other hand, a reverse bias serves to increase the barrier to $V_o + V_r$, making flow
Figure 2.4: Schottky junctions under bias
of electrons from the semiconductor to the metal negligible. In both cases, the flow of electrons from the metal to the semiconductor faces the barrier \( \phi_m - \chi \). The diode equation can be derived and is of the form

\[ I = I_o(e^{qV/kT} - 1). \]  

(2.5)

However, in this case, the reverse saturation current \( I_o \) is not as easily derived as in the p-n junction. One aspect that we can predict intuitively, however, is that the saturation current should depend on the magnitude of the barrier \( \phi_b \) for electron injection from the metal into the semiconductor. This barrier, which is \( \phi_m - \chi \) for the ideal case discussed above, is unaffected by the bias voltage. Assuming the probability of an electron in the metal to surmount this barrier to be given by a Boltzmann factor, we can predict

\[ I_o = Ke^{-q\phi_b/kT}, \]  

(2.6)

where \( K \) is a constant of proportionality.

The same diode equation applies to the metal-p type semiconductor junction of Figure 2.3. In this case forward voltage is defined with the semiconductor biased positively with respect to the metal. Forward current increases as this voltage lowers the potential barrier to \( V_o - V \) and holes flow from the semiconductor to the metal. Reverse voltage increases the barrier to hole flow and the current flow is negligible.

In both cases, the Schottky barrier diode is rectifying, with significant current flow in one direction and very little current in the other direction. Also, it is to be noted
that the forward current in each case is due to the injection of majority carriers. This leads to better high frequency properties and faster switching speeds.

When semiconductor technology was just getting started, rectifying contacts were made by simply pressing a metal wire against the surface of the semiconductor. Metal-semiconductor contacts are now made by evaporating the metal on the semiconductor surface in a vacuum chamber, which is the way we deposit the contacts on our ZnSe films.

### 2.4 Depletion Capacitance of Schottky Diodes

The depletion capacitance is the capacitance observed when a reverse bias is applied to the semiconductor (which is when the depletion region is formed). The measurement of capacitance with varying voltage can be used to determine the doping profile (i.e., how the doping varies with depth) in the semiconductor. It is convenient to consider a metal-semiconductor Schottky diode as a one-sided junction; the formulae are equally applicable to both cases.

Consider Figure 2.5, which shows the spatial variation of the energy bands and the Fermi energy in a $p$ type semiconductor in the vicinity of a metal Schottky surface layer for two values $V_{d1}$ and $V_{d2}$ of applied reverse-bias voltage, with $V_{d1} > V_{d2}$.

The distance $x$ is measured from the metal:semiconductor interface, and $x_{d1}$ and $x_{d2}$ are the depletion distances for $V_a$ equal to $V_{d1}$ and $V_{d2}$ respectively. It is clear that increasing the applied voltage from $V_{d1}$ to $V_{d2}$ causes the movement of charges,
Figure 2.5: Space charge regions in Schottky junctions
leaving uncompensated negatively charged acceptor ions \( \text{N}_a^- \). The junction therefore acts as an electrical capacitor, of capacitance equal to \( Q/V_a \), where \( Q \) is the charge stored in the depletion region, and of small-signal (differential) capacitance \( C_a \) equal to \( dQ/dV_a \).

If the doping density \( N_a \) of the semiconductor is independent of distance \( x \), then the charge \( Q \) stored in a depletion region of width \( x_d \) is \( N_a x_d A \), where \( A \) is the junction area, and therefore from Equation 2.4 we get the value of \( Q \) to be

\[
Q = A (2\epsilon_r \epsilon_0 N_a (V_{bi} + V_a))^{0.5}
\]

(2.7)

and \( C_a \) is given by the expression

\[
C_a = dQ/dV_a = 0.5 A (2\epsilon_r \epsilon_0 N_a / (V_{bi} + V_a))^{0.5} = \epsilon_0 \epsilon_r A / x_d,
\]

(2.8)

which is the formula for the capacitance of a parallel plate capacitor with the plates separated by \( x_d \).

The more general case of doping is assumed in Figure 2.6, where the doping concentration varies with distance \( x \). In these measurements, the capacitance is determined by superimposing a small-amplitude ac voltage \( v \) on the dc voltage \( V \). The ac voltage can have frequencies from 2KHz-1MHz and has an amplitude of about 30 mV.

Consider the diode to be biased to a dc voltage \( V \) plus a sinusoidal ac voltage. Imagine the ac voltage increasing from zero to a small positive voltage adding a charge increment \( dQ_m \) to the metal contact. The charge increment \( dQ_m \) must be balanced
Figure 2.6: Depletion region in non-uniformly doped Schottky junction

by an equal semiconductor charge increment $dQ_s$ for overall charge neutrality, where $dQ_s$ is given by

$$dQ_s = -eAN_a(W)dW.$$  \hspace{1cm} (2.9)

The charge increment $dQ_s$, shown in Figure 2.6, comes about through a slight increase in the width of the depletion region (which contains negatively charged acceptors). Using the equations referenced earlier, we get

$$C = -\frac{dQ_s}{dV} = eAN_a(W)\frac{dW}{dV_a}. \hspace{1cm} (2.10)$$
The capacitance of a reverse-biased junction, when considered as a parallel plate capacitor, is expressed as

$$C = K_d \varepsilon_0 A/W.$$  \hfill (2.11)

Differentiating equation 2.10 with respect to voltage we get

$$N_a(W) = -\frac{C^3}{eK_d \varepsilon_0 A^2 (dC/dV)},$$  \hfill (2.12)

which can also be written as

$$N_a(W) = \frac{2}{eK_d \varepsilon_0 A^2 [d(1/C^2)/dV]},$$  \hfill (2.13)

using the identity $d(1/C^2)/dV = -(2/C^3)dC/dV$. Using the equations above together with the expression for depletion width,

$$W = K_d \varepsilon_0 A/C,$$  \hfill (2.14)

we can get the doping profile of the semiconductor. The doping concentration is obtained from a C-V curve by calculating the slope $d(1/C^2)/dV$. The depth at which the doping concentration has been evaluated is found by using Equation 2.4. If the doping concentration is uniform throughout the sample, the slope $d(1/C^2)/dV$ will be a straight line.

### 2.5 Ohmic Contacts

In many instances we wish to have an ohmic metal-semiconductor contact— one that has a linear I-V characteristic in both biasing directions. We need ohmic contacts
when we want the contact to have minimal resistance and to have no tendency to rectify signals.

Ideal metal-semiconductor contacts, having no surface states, are ohmic if $\phi_m < \phi_s$ for a n type semiconductor or if $\phi_m > \phi_s$ for a p type semiconductor (refer to Figure 2.7).

In the n type case, as shown in Figure 2.7, the Fermi levels are aligned at equilibrium by transferring electrons from the metal to the semiconductor. This raises the semiconductor electron energies (lowers the electrostatic potential) relative to the metal at equilibrium. The barrier to electron flow between the metal and the semiconductor becomes small and is easily overcome by a small voltage. Similarly, the case $\phi_m > \phi_s$ for a p type semiconductor results in easy flow of holes across the junction. Unlike the Schottky diode discussed above, no depletion occurs in the semiconductor in these cases since the electrostatic potential required to align the Fermi levels at equilibrium calls for accumulation of majority carriers in the semiconductor.

One way of forming ohmic contacts is by doping the semiconductor heavily in the contact region. Then, if a barrier exists at the interface, the depletion width is small enough to allow carriers to tunnel through the barrier. For example, Au containing a small percentage of Zn can be alloyed onto p type GaAs, forming a p+ layer at the semiconductor surface and an excellent ohmic contact. Similarly n type GaAs requires a n+ layer in contact, which can be achieved by alloying Au containing a small amount of Ge.
Figure 2.7: Band diagrams for Ohmic junctions
2.6 Photoluminescence

Photoluminescence (PL) is luminescence excited by photons. PL detects optical emission when an excited state relaxes to a lower state. Photoluminescence spectroscopy is a sensitive method for detecting transitions (both intrinsic and impurity-related) between energy levels in semiconductors.

An imperfection introduced into a crystal disrupts the periodic structure of the lattice and changes the electrical and optical properties of the material. Electronic states are produced in the band gap by these imperfections. The location of these states depends on the ionization energy of the defect. Some of these states are radiative centers, while some decay non-radiatively. An analysis of the spectrum of radiative emission (which is what PL accomplishes) yields information on the energy levels of the radiative impurity and defect levels, and thus of the quality of the material.

To observe these emissions, the electrons must be excited to energies greater than the defect level by irradiating the material with photons of energy greater than the band gap. For ZnSe, which has a band gap of 2.67 eV, a He-Cd laser operating at 325 nm may be used. Also, to prevent thermal ionization of optically active centers and to minimize spectral line broadening by lattice vibrations, PL must be performed with the sample at very low temperatures (8°K in our case). Electrons are excited from the valence band to the conduction band. They then recombine at an active center yielding a radiative emission of characteristic wavelength. The radiative
emission is analyzed with a spectrometer to obtain the PL spectrum. The locations of the peaks in the PL spectrum yield information on the quality of the sample.

The various emissions observed in ZnSe films are:

- Free Exciton: This is the transition resulting from the interaction of a free electron and a free hole. It is the emission with the highest energy, typically 442.5 nm.

- Donor Bound Exciton: This emission arises from excitons bound to donors. It occurs at 2.797 eV (443.3 nm).

- Acceptor Bound Exciton: The acceptor bound exciton emission, which occurs at 444.4 nm, indicates the presence of acceptors.

- Donor-Acceptor Pair Recombinations: Materials having both donors and acceptors exhibit this transition between a donor and an acceptor. This occurs at 2.698 eV (459.2 nm), with a phonon-coupled peak at 2.677 eV (463 nm). The presence of this peak indicates compensation.

- Deep Level Emission: There are several deep level emissions that are observed in poor quality ZnSe films, and these are mainly due to undesirable defects or impurity levels. The PL peaks noticed are:

  - 'Y' line emission at 2.6eV (476 nm) which are indicative of defects like threading dislocations.
- 'S' or 'M' lines at 2.5 eV (495 nm), often seen with phonon coupled peaks.

- Broad-band emission centered about 2.3 to 2.4 eV (516 to 539 nm), attributed to unintentional incorporation of copper during growth.

- Self activated (SA) broad band luminescence between 2.14 and 1.97 eV (579.4 to 629.4 nm) related to Ga or Zn complexes.
Chapter 3

Experimental Apparatus

The experimental apparatus has been discussed in exhaustive detail in the thesii of Paul Gillespie [41] and Gregory Shinn [42]. Here an overview is presented.

3.1 Growth System

This is a custom designed CVD reactor. A schematic is shown in Figure 3.1. It has four major subsystems which are described below.

3.1.1 Hydrogen carrier gas purification

The extra-dry grade hydrogen used in our experiments is purified by passing it through a palladium alloy barrier in a Johnson-Matthey commercial purification unit. Prior to entering this purifier, the gas is filtered through particle filters.

3.1.2 Metalorganic Sources and Bubbler Transport Systems

The metalorganic bubbler system is shown in Figure 3.2. The source gases, dimethyl zinc (DmZn) and diethyl selenide (DeSe), are stored in stainless steel bubblers with shut-off valves. These metalorganics are highly pyrophoric, and thus extreme caution is taken to ensure that the system is leak-tight and that any unreacted material is
Figure 3.1 MOCVD System
Figure 3.2: The Bubbler System

destroyed. Both sources are high vapor pressure liquids, with specific pressures at specific temperatures (the values of which can be ascertained from graphs supplied by the manufacturers). To maintain metalorganic vapor pressures at about 110 Torr, the DmZn bubbler is kept partially submerged in a constant temperature bath at -2.5°C, while the DeSe bubbler is maintained at a temperature of 55°C for the same purpose. The mass flow controllers are set to flow rates of 20 sccm of hydrogen for the DmZn bubbler and 200 sccm for the DeSe bubbler.

3.1.3 MOCVD Reactor

The reactor is as shown in Figure 3.3. The source gases enter through inlets and mix
before entering the growth region. The growth section consists of a 4" outer diameter tube with three windows to allow for introduction of radiation, and a 3.5" stainless steel tube insert to allow for purging of windows. Effective purging of windows is extremely important to prevent deposition of material on the windows. Mass flow controllers are used to accurately control the purge rates. The substrate is mounted on a 1" by 6" rectangular stainless steel heater suspended horizontally in the center of the reactor on the end of a stainless steel tube. Stainless steel clips are used to hold the GaAs wafer in place. Growth temperature is controlled by regulating the power to the heater by using a variable power transformer.
3.1.4 Exhaust System

The exhaust system is necessary to ensure that unreacted metalorganics and potentially toxic by-products are removed before release of the exit stream to the atmosphere. A bubbler system at the end of the reactor removes solid particles. The bubbler also prevents backstreaming of air into the reactor in the event of a failure during growth. An inverse bubbler trap, located immediately upstream, traps any oil forced backstream. The gases then pass through a pyrolysis furnace, maintained at 850°C. This destroys unreacted metalorganics. Finally, a bed of potassium hydroxide impregnated charcoal positioned at the inlet of the mechanical pump adsorbs any hydrogen selenide that might have been generated as a by-product.

3.2 Equipment used for annealing and deposition of contacts

The furnace used for annealing is shown in Figure 3.4. A quartz furnace tube having aluminum caps held snug by O-rings is used to allow for anneals up to 850 degrees celsius. A Omega CN5000 K2 temperature controller is used to maintain the desired temperature. To ensure a reducing environment, a stream of a forming gas mixture (95% N₂, 5% H₂) passes through the furnace tube, as shown in the figure.

The contacts are developed by a photolithographic process, described in detail in the following chapter. Gold was evaporated in a vacuum chamber at a pressure of
2×10⁻⁶ Torr using a tungsten boat. For evaporation of SiO, a special boat, as shown in Figure 3.5, is used.

3.3 Apparatus used in C-V and I-V measurements

Small signal capacitance measurements are made using a HP4284A LCR meter, in the configuration shown in Figure 3.6. This has the capability of making measurements at frequencies from 20 Hz to 1 Mhz with up to +/- 42 V DC bias. The sample is mounted on a vacuum chuck with Micromanipulator probe tips making contact with the sample. The signals go through BNC feedthroughs which were insulated from the ground. The outer shield conductors form the return path for the measurement.
Figure 3.5: Boat used for SiO evaporation

Figure 3.6: Apparatus used for CV measurements
signal current. The same current flows through both the central conductors and the outer shield conductors. Thus no external magnetic fields are generated as the magnetic fields formed by the outer and inner currents cancel each other. There are four probes out of the HP4284, to allow for measurements in the standard four-point probe method, which minimizes parasitic contact and spreading resistances. However, we have modified the four point probe to a two terminal configuration as shown in Figure 3.6. This made measurements easier as we eliminate two probes. Some accuracy is sacrificed in doing so, but the percentage error is small as we are measuring large reactances (small capacitances) and the contact resistances are small.

There is some amount of stray capacitance associated with the exposed probe tip and the vacuum chuck, but these could be minimized by the correction procedures available with the CV bridge. A better way to account for stray capacitance is to measure the stray capacitance of the chuck and the probe, and then subtract this value from the data acquired in the computer. The cable capacitance is minimized by matching the connecting cable and type.

Data acquisition is entirely computer controlled through a Texas Instruments Personal Computer connected via a GPIB interface. The computer program enables the user to choose scan range, step and hold times, and frequency of operation. The data, stored on a disk, is transferred to a Macintosh and the $1/C^2$ vs $V$ plots are obtained.
3.4 Apparatus for photoluminescence

Figure 3.7 shows the setup used for photoluminescence experiments. A Helium-Cadmium laser radiating at 325 nm is used as the excitation source for PL measurements. The beam passes through a UV grade quartz prism which removes the
visible plasma lines from the UV He-Cd laser beam. The optical path of the beam is then lengthened by reflections off three dielectric mirrors to enable spatial filtering of the plasma lines from the beam. A mechanical chopper C1 modulates the beam to permit phase-sensitive detection using a lock-in amplifier, so as to reduce the background noise. The detector is sensitive only to light in phase with the chopper. The laser beam is focussed onto the sample by lens L1. The sample is mounted on a copper cold finger of a Cryogenics refrigeration unit, fastened to the block by rubber cement. The cryostat is capable of temperature control down to 8°K. The cold finger is surrounded by a highly reflective radiation shield to prevent heat transfer from the outside by radiation. Light passes into and out of the sample through holes in the radiative shield. A mechanical pump is used to evacuate the cryostat, so as to prevent condensation of water vapor and gases in the air on the sample. The luminescence from the sample is collected normal to the sample, and directed to the spectrometer by lens L2 of focal length 15 cm. A low pass UV filter placed in front of the spectrometer prevents any scattered UV light from the 325 nm laser from entering the spectrometer. The intensity of the luminescence can be reduced by using neutral density filters (NDFs).

The spectrometer has three gratings: 2400 grooves/mm, 1200g/mm and 600g/mm. The gratings can be chosen via the software. A Texas Instruments personal computer is used to control the spectrometer through a RS 232 interface. The data acquisition is computer controlled. The wavelength range, grating desired, data increment and
step times can all be controlled through the software. The data is recorded as a string of intensities, and can be plotted using a plotting program.
Chapter 4

Experiments Performed and Results

4.1 Overview

Experiments have been performed to obtain a method that yields p doped ZnSe, and reactor conditions have been optimized to obtain the best quality (with the heaviest doping concentration) p doped ZnSe. The films are characterized optically (by observing their photoluminescence) as well as electrically (by C-V techniques). Several growth parameters were kept constant from growth to growth. These parameters were:

- Mass flow rates of hydrogen and metalorganics
- Total chamber pressure
- Growth Procedures- pump out, heating and cooling rates, etc.
- Sample mounting, geometry, preparation, etc.

The specifications are listed in the Table 4.1. Most of the parameters kept constant here had been previously optimized [42]. The ratio DeS:DmZn was maintained at 10:1 because most epitaxial growth processes are believed to be limited by the transport of the group II species. Hydrogen flow ratio of 10:1 was maintained in the constant
<table>
<thead>
<tr>
<th>Mass Flow Rate DMZ</th>
<th>2.16 sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass Flow Rate DeS</td>
<td>25.23 sccm</td>
</tr>
<tr>
<td>Mass Flow Rate total</td>
<td>2017.39 sccm</td>
</tr>
<tr>
<td>Se/Zn Ratio</td>
<td>11.67:1</td>
</tr>
<tr>
<td>H₂ Dilution</td>
<td>73.6:1</td>
</tr>
<tr>
<td>Velocity(inner tube)</td>
<td>23.9 cm/sec</td>
</tr>
<tr>
<td>Total chamber pressure</td>
<td>100 Torr</td>
</tr>
</tbody>
</table>

Table 4.1: Constant Parameters

temperature bubblers yielding the values listed in the table above. The main component of the total flow was the hydrogen carrier gas. The velocity of flow in the inner tube was chosen such that the flow was laminar as per classical hydrodynamics. The flow in the chamber can be modeled as laminar flow between two parallel plates. The velocity of the H₂ purge gas in the outer tube was chosen such that it matched closely the velocity in the inner tube. The flow rates of the purge gases were maintained constant at levels that enabled adequate window cleanliness.

4.2 Growth Procedures

2" wafers of GaAs were cleaved into four quarters before they were used for growth, because they are expensive. Cleaving was done by placing the wafer on a hard surface, and forcing a razor blade edge onto one of the flats of the wafer such that a crack was initiated and propagated along the length of the wafer. This method left the wafers clean. The wafers were held in good contact with the stainless steel substrate holder by two steel clips. Before growth, the chamber was evacuated for at least 8 hours
using a diffusion pump. Hydrogen was then passed through the reactor for about 20 minutes to remove any residual oxygen. Then the temperature was ramped up slowly (turning the variac up by 5 Volts every 10 minutes) to 600°C to remove the GaAs native oxide. If this procedure was not performed, very poor quality films were obtained, as seen in a typical PL plot in Figure 4.1. Such films exhibit PL spectra dominated by defect peaks - the defect peak at 476.5 nm and the self-activated defect peak centered around 548.5 nm.

The temperature was then ramped down to the growth temperature. After the growth was over, hydrogen flow was maintained for about half an hour after the metalorganic sources were shut off, until the substrate temperature was about 50°C. Before opening up the reactor to remove the film, three cycles of pumpout followed by helium backfills were necessary to remove any harmful Se byproducts that might remain. Proper protective clothing was worn.

4.3 Annealing Procedures

Annealing was performed in the furnace described in the previous chapter. The ZnSe surface started to degrade when anneals were done at temperatures greater than 500°C. To enable anneals at higher temperatures, a thin layer of SiO was deposited on the surface. The special boat described in Chapter 3 was used to prevent the SiO from spilling out of the boat. SiO is very hard and abrasive, but it can be crushed easily because of the existence of a network of stress fissures throughout the solid. A
Figure 4.1: PL of a sample where the native oxide was not removed
small amount of powdered SiO was placed in the boat and loaded into the vacuum belljar. Evacuation of only $1 \times 10^{-4}$ mm Hg was enough for SiO deposition. A current of about 300 Amperes was found to be necessary for SiO deposition. Using the thickness monitor, about 1000 Angstroms of SiO was deposited. Then the sample was left in the bell-jar for an hour, until it cooled off, taken out, and was then ready for annealing. Annealing was done in a forming gas environment. The sample was placed in a quartz plate that fits in the anneal furnace tube. First, the desired set temperature was reached, then the forming gas supply was opened. Then one of the Al caps of the furnace tube was opened; the sample (sitting on the quartz plate) was slowly pushed into the tube, and then the Al cap put back on. The temperature was maintained for about 45 seconds. Then the heater was switched off and the furnace tube pushed out so that the sample was positioned right above the cooling fan. The sample was allowed to cool in the forming gas environment for about an hour. Then the SiO cap was removed by HF treatment. HF preferentially etched away oxide, removing the SiO in this case. The sample was then washed with deionized water, cleaned with acetone and methanol, and then was ready for contact deposition.

4.4 The Planar Schottky Technique

This is the technique used for C-V measurements for samples grown on semi-insulating GaAs. C-V measurements require a contact pattern as shown in Figure 4.2. The dark regions indicate areas where Au is deposited, and the annular clear region is exposed
ZnSe. The island dots form the gate contacts (to which the probe voltage is applied) and the large expanse of metal all around them is the ground plane contact. This creates a circuit that has two Schottky capacitors in series. Capacitance scales as area, and since the ground plane has an area much larger than the gate, the gate capacitance is much smaller. With two capacitances in series, one much smaller than the other, the net capacitance is very close to the small capacitance (ref: The net capacitance $C_{\text{net}}$ formed by two capacitors $C_1$ and $C_2$ in series is given by $1/C_{\text{net}} = 1/C_1 + 1/C_2$). The net capacitance is what we measure when we use the HP4284 and apply voltage to the probe on the gate contact and use the probe on the ground plane as the return path to the 4284. In effect we are measuring a metal-semiconductor structure of the kind described in Chapter 2, and the equations listed there are applicable. One advantage of this method is that conduction across the ZnSe/GaAs heterojunction can be ignored. This model assumes that the region of semiconductor under the
gap between the contacts acts as a wire. Thus, the gap between the electrodes (the annular region in between the two circles) should be kept a minimum, ensuring that the series resistance added by the semiconductor is kept to a minimum. The validity of this model was checked by trying this technique on GaAs wafers of known carrier concentration, and in each case the experimental results closely matched the specified values. (Refer to Table 4.2) Several different mask geometries were tried out, with gate diameters ranging from 0.01 inch to 0.08 inch, and a gap of about 0.001 inch between the contacts. The contacts were deposited using a photolithographic lift-off procedure. The basic steps involved are:

- Spin the photoresist (S 1813) on the wafer for 25 secs at 4500 rpm
- Soft bake at 90 deg C for 30 minutes, then cool to room temperature
- Expose through mask to UV light for 10 secs
- Develop with MF 355 developer solution for about 45 secs
- Load sample in the vacuum evaporator and pump down to at least $2 \times 10^{-6}$ Torr
- Evaporate metal (Au) onto surface over photoresist structures

<table>
<thead>
<tr>
<th>Substrate Type</th>
<th>Concentration Specified by Manufacturer</th>
<th>Concentration Calculated Experimentally</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>n GaAs</td>
<td>$4.2 \times 10^{18}/\text{cm}^3$</td>
<td>$3.96 \times 10^{18}/\text{cm}^3$</td>
<td>5.7</td>
</tr>
<tr>
<td>n GaAs</td>
<td>$4.2 \times 10^{18}/\text{cm}^3$</td>
<td>$4.31 \times 10^{18}/\text{cm}^3$</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 4.2: Planar Schottky Method applied to GaAs wafers
• Remove sample from the evaporator and then place it in acetone

• Place in ultrasound cleaner till all undesired metal is removed. Now the sample is ready for C-V analysis using the HP4284.

4.5 Geometries used with n and p type GaAs substrates

ZnSe samples were also grown on n and p type GaAs substrates. On the top (ZnSe) surface, circular gold dots were evaporated, forming Schottky barriers. The bottom surface (GaAs) had ohmic contacts evaporated on them. For p GaAs, this is achieved by evaporating an alloy of about 5% Zn and 95% Au, and then annealing at 450°C for 5 min in a reducing atmosphere. Good ohmic behavior is observed only after annealing. Ohmic contacts to n GaAs are made by evaporating an alloy comprising if 80% Au and 20% Ge, and annealing rapidly at 400°C for 30 seconds, then cooling to room temperature in a forming gas atmosphere.

With conducting GaAs substrates, current flows through the ZnSe/GaAs heterojunction. But again, because the ohmic contact on the bottom of GaAs covers the entire wafer, we have the same situation, as before, of having two very disparate capacitors in series. The net capacitance that we measure is very nearly equal to the top capacitor (the Au:ZnSe Schottky capacitor), as it is much smaller in area.

Samples grown on conducting (n and p type) GaAs substrates showed exactly the same I-V, C-V and PL characteristics as the samples grown on semi-insulating
GaAs. This proves that we are indeed analyzing the properties of ZnSe (and not of the GaAs), and also validates our capacitor models.

4.6 C-V and I-V measurements

C-V measurements were done using the IIP4284. The program used is CVF, which is in the directory C/APO. The PC runs on a version of BASIC called BASICA; the commands are the same as BASIC. The program CVF is menu-driven, and enables the user to choose the various scan parameters. The usual parameters chosen were: hold time of 2 seconds, step time of 2-5 seconds (depending on how noisy the curve looks—a longer step time leads to smoother curves) and a step voltage of 0.2 Volts. Multi-frequency scans are possible using this setup, from 20Hz to 1MHZ. The data obtained is stored as a string and is later transferred to a plotting program (Kaleidagraph on the Macintosh) for plotting and curve fitting.

The I-V curves were obtained in a similar fashion, using the program IV4140B in the directory C/APO. Step sizes of 0.2 V were used, and the step time used was 0.25 seconds. Data was collected and analyzed in a manner similar to that used for C-V measurements.

4.7 Results after annealing

Samples showed remarkable changes in electrical properties after annealing. Samples that were not annealed did not show any conclusive p-type behavior. As seen in
Figure 4.3, the C-V curves of these samples did not show evidence of any active carriers. The range of capacitance values observed indicated a fully depleted ZnSe layer (using equation 2.8 and values for ZnSe film thickness calculated using an interferometric technique). Figure 4.4 shows the C-V curves of the same sample after annealing at 700°C for 30 secs. This sample shows clean, clear p type behavior. The

![Graph of C vs V](image)

**Figure 4.3: Typical C vs V for a sample before annealing**

$1/C^2$ vs V curve, shown in Figure 4.5, shows a good straight line fit, indicating that the doping density is uniform. The I-V curve is plotted in Figure 4.6, and is what is expected with our planar contact geometry. Since we have two back-to-back Schottky diodes, we expect to see very little current through the contacts. This is indeed the
Figure 4.4: Typical C vs V for an annealed sample

case- the current observed is extremely small. All of our samples exhibit these kinds of C-V and I-V curves, indicating good p type behavior. To determine the dependence of p doping on annealing temperature, a series of annealings were performed at various temperatures. Clear p type behavior was observed for anneals done at temperatures above 300°C. Samples annealed at 200°C did not exhibit p type behavior. The dependence of carrier concentration on annealing temperature is detailed in Table 4.3. Figure 4.7 plots the dependence of carrier concentration on annealing temperature. $T_{\text{growth}}$ is the temperature at which the growth is performed, $t_{\text{growth}}$ is the time for which growth is done, in minutes, $T_{\text{anneal}}$ is the annealing temperature,
Figure 4.5: Typical $1/C^2$ vs $V$ for an annealed sample

<table>
<thead>
<tr>
<th>$T_{growth}$ (°C)</th>
<th>NH$_3$ (sccm)</th>
<th>$t_{growth}$ (min)</th>
<th>$T_{anneal}$</th>
<th>Conc/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>475</td>
<td>2</td>
<td>15</td>
<td>300</td>
<td>$1.2 \times 10^{17}$</td>
</tr>
<tr>
<td>475</td>
<td>2</td>
<td>15</td>
<td>400</td>
<td>$4.4 \times 10^{17}$</td>
</tr>
<tr>
<td>475</td>
<td>2</td>
<td>15</td>
<td>450</td>
<td>$3.6 \times 10^{17}$</td>
</tr>
<tr>
<td>475</td>
<td>2</td>
<td>15</td>
<td>500</td>
<td>$2.7 \times 10^{17}$</td>
</tr>
<tr>
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<td>2</td>
<td>15</td>
<td>575</td>
<td>$7.4 \times 10^{17}$</td>
</tr>
<tr>
<td>475</td>
<td>2</td>
<td>15</td>
<td>650</td>
<td>$5.4 \times 10^{17}$</td>
</tr>
<tr>
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<td>15</td>
<td>675</td>
<td>$6.0 \times 10^{17}$</td>
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<td>15</td>
<td>725</td>
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</tr>
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<td>15</td>
<td>750</td>
<td>$7.1 \times 10^{17}$</td>
</tr>
<tr>
<td>475</td>
<td>2</td>
<td>15</td>
<td>815</td>
<td>$1.5 \times 10^{17}$</td>
</tr>
</tbody>
</table>

Table 4.3: Concentration Dependence on Anneal Temperatures
and the NH$_3$ flow column gives the ammonia flow rate in standard cubic centimeters per minute (sccm).

No particular trend in the values of carrier concentration was observed with changing the annealing temperature, as long as the temperature was above the threshold of 300°C. The slight variations in doping density observed are probably due to variation in growth procedures, like the variation in times for which the chamber was evacuated by the diffusion pump prior to growth, and the time for which the chamber was left open to the atmosphere while taking out a sample and loading a new one. Thus, the conclusion that can be made is that a threshold annealing temperature of 300°C
is required to electrically activate the carriers. Carrier concentration appears to be independent of temperature of annealing for temperatures greater than this threshold temperature of 300°C.

### 4.8 Dependence of doping on growth temperature

The growth temperature was varied and its effect on the doping density is shown in Table 4.4. The dependence is plotted in Figure 4.8. The doping density in the ZnSe films is found to have a very strong dependence on the growth temperature. It peaks at about 475°C, and drops off remarkably as the temperature is increased.
<table>
<thead>
<tr>
<th>$\text{NH}_3$ (sccm)</th>
<th>$t_{\text{growth}}$ (min)</th>
<th>$T_{\text{anneal}}$</th>
<th>$T_{\text{growth}}$</th>
<th>Conc/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>15</td>
<td>700</td>
<td>425</td>
<td>$3.6 \times 10^{14}$</td>
</tr>
<tr>
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<td>15</td>
<td>700</td>
<td>455</td>
<td>$7.8 \times 10^{16}$</td>
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<td>700</td>
<td>475</td>
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<td>510</td>
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<td>700</td>
<td>525</td>
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<tr>
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<td>700</td>
<td>550</td>
<td>$2.7 \times 10^{14}$</td>
</tr>
</tbody>
</table>

Table 4.4: Concentration Dependence on Growth Temperatures

Figure 4.8: Doping Density vs Growth Temperature
or decreased. This optimum temperature is higher than the temperature at which some other groups grow their samples; some groups report growth at temperatures as low as 250°C. But, these groups use atomic N as the dopant. Our higher optimum growth temperature may be due to our need to dissociate NH₃ to produce N. Also, the temperature indicated is the thermocouple temperature, which we expect to be greater than the temperature on the growth surface.

### 4.9 Dependence of doping on NH₃ flow rate

Experiments were performed to determine the effect of changing the flow rate of the NH₃ gas. The mass flow controller used to control the flow of ammonia is rated for operation up to 10 sccm, and Table 4.5 tabulates the results of changing the flow rates using this MFC. The dependence of doping density on NH₃ flow rate is plotted in Figure 4.9. The optimum flow rate is about 2 sccm. Changing the flow rates from this value leads to a decrease in the doping density. While the mechanism of nitrogen incorporation is not clear, we can conclude that the optimum condition is a flow rate of 2 sccm of NH₃.

<table>
<thead>
<tr>
<th>t&lt;sub&gt;growth&lt;/sub&gt; (min)</th>
<th>T&lt;sub&gt;anneal&lt;/sub&gt;</th>
<th>T&lt;sub&gt;growth&lt;/sub&gt;</th>
<th>NH₃ (sccm)</th>
<th>Conc/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>700</td>
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<td>1</td>
<td>4.9 × 10¹⁷</td>
</tr>
<tr>
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<td>7.9 × 10¹⁷</td>
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<td>15</td>
<td>700</td>
<td>475</td>
<td>3</td>
<td>5.8 × 10¹⁷</td>
</tr>
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<td>700</td>
<td>475</td>
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<td>700</td>
<td>475</td>
<td>8</td>
<td>2.8 × 10¹⁶</td>
</tr>
</tbody>
</table>

Table 4.5: Concentration Dependence on NH₃ flow rate
Figure 4.9: Doping Density vs NH$_3$ Flowrate

4.10 Effect of broad-band illumination on doping density

Several researchers [41,42] have investigated the effect of having a broad-band light source irradiate the substrate during growth. It has been found to increase the growth rate. We have conducted experiments where we irradiated the surface directly using a Xe lamp. The samples thus grown have the doping densities listed in Table 4.6. Figure 4.10 shows this dependence. The data seems to indicate increasing nitrogen incorporation with increasing illumination intensity.
<table>
<thead>
<tr>
<th>$t_{growth}$ (min)</th>
<th>$T_{anneal}$</th>
<th>$T_{growth}$</th>
<th>$\text{NH}_3$ (sccm)</th>
<th>$I_{\text{bulb}}$ Intensity (mW/cm$^2$)</th>
<th>Conc. /cm$^3$</th>
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<tr>
<td>15</td>
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<td>75</td>
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<td>225</td>
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<td>700</td>
<td>475</td>
<td>2</td>
<td>300</td>
<td>$6.5 \times 10^{17}$</td>
</tr>
</tbody>
</table>

Table 4.6: Effect of direct broad-band radiation

![Doping Density dependence on UV Illumination](image)

Figure 4.10: Doping Density Dependence on UV Illumination
4.11 Concentration dependence on laser irradiation

Gillespie and Shinn [41,42] have observed improved growth rates when a laser beam was focussed parallel and near the substrate (but not hitting the substrate) during growth. Figure 4.11 shows the arrangement used. An ArF laser emitting at 193 nm was used. Effects of such laser irradiation on doping density are as shown in Table 4.7. The laser was operated at 100 mJ with a repetition rate of 10 Hz. The laser seems to have an adverse affect on the doping density of ZnSe films. Laser irradiation possibly changes the mechanism of nitrogen incorporation such that the nitrogen
<table>
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<th>Laser Power (mJ)</th>
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<th>T\text{\textsubscript{growth}}</th>
<th>NH\textsubscript{3}(sccm)</th>
<th>Conc/cm\textsuperscript{2}</th>
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</thead>
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<tr>
<td>100</td>
<td>650</td>
<td>475</td>
<td>2</td>
<td>1.5 \times 10^{16}</td>
</tr>
<tr>
<td>50</td>
<td>700</td>
<td>475</td>
<td>2</td>
<td>2.7 \times 10^{15}</td>
</tr>
<tr>
<td>25</td>
<td>750</td>
<td>475</td>
<td>2</td>
<td>4.5 \times 10^{15}</td>
</tr>
</tbody>
</table>

Table 4.7: Effect of ArF laser irradiation

atoms become strongly bonded to interstitial atoms. These bonds cannot be broken by the annealing process, and hence the films remain passivated.

4.12 PL procedures and results

4.12.1 PL procedures

The PL chamber must be at about room temperature before it is opened up to the atmosphere, to prevent condensation of water on the sample. The chamber can be backfilled with dry Nitrogen if rapid heating up to room temperature is necessary. Samples are fastened to the copper block using drops of rubber cement. After the cement has dried, the copper cold finger is remounted and the cryostat housing put back in place. The mechanical pump is turned on and the cryostat evacuated to about 100 mTorr. The cryostat compressor is turned on, allowed to warm up for about 10 minutes and then the cold head refrigerator turned on. It takes about 90 minutes for the temperature to cool down to about 8\textdegree K. The laser is then turned on, and a bright blue spot is usually visible where it hits the sample. The luminescence
is imaged onto the spectrometer slit using the lenses. The spectrometer is tuned to a large wavelength peak and the filters placed in the path of the beam such that the intensity remains on scale. The phase of the lock-in is adjusted to maximize the signal.

The data is recorded using the program ACTONPL. Slit widths and gratings must be chosen with care. For the long (435-635 nm) scans, a slit width of 60 microns, grating 2 (with 1200 g/mm), and a data step size of 0.50 nm is chosen. Grating 1 (2400g/mm), a slit width of 25 microns and data increments of 0.20 nm is used for the shorter, high-resolution scans.

4.12.2 PL results

The undoped films exhibited the PL spectra as shown in Figure 4.12. The dominant peak is the donor-bound exciton (DBE) peak at about 443.5 nm. This peak is characteristic of donor levels. ZnSe takes on an n type characteristic when grown undoped, hence this peak is expected. There are no acceptor-bound exciton (ABE) peaks or Donor-acceptor Pair (DAP) peaks- these peaks are characteristic of acceptor levels.

Most of the p doped films with good carrier concentration exhibited typical PL spectra shown in Figure 4.13. The dominant peak is the DAP peak at about 460.5 nm, with a phonon coupled DAP peak at 465.5 nm. The ABE and the DBE peaks appear as one broad peak centered around 444 nm. Typically, the DAP peak is of a much larger magnitude than the ABE and DBE peaks, and often it is the only peak
Figure 4.12: Typical PL spectra of an undoped sample

observable on a common scale. This data correlates very well to that reported by the 3M group that used a MBE technique to obtain the highest doping density on p ZnSe. They too observe a dominant DAP peak in samples that had the highest doping densities. As postulated by them, the DAP peak indicates compensation of acceptors, but they have used SIMS analysis to prove that concomitant with this increase in compensation is an increase in the amount of nitrogen incorporated into the films. They have demonstrated nitrogen incorporation of as much as $1 \times 10^{19}$/cm$^3$, as indicated by SIMS, though C-V analysis showed that only $1 \times 10^{18}$/cm$^3$ of these carriers were electrically active. Thus, it can be concluded that we are looking at
Figure 4.13: PL spectra of a typical doped film
the same situation. The DAP dominant peak indicates compensation, but we have enough nitrogen incorporated into our films to permit the high \(7.9 \times 10^{17}/\text{cm}^3\) doping densities. We will be obtaining numerical values of the amount of nitrogen incorporated in our films by utilizing SIMS facilities at Texas Instruments Labs, Dallas.

Comparison of PL spectra of films grown at different temperatures shows that the best quality films are obtained at 475°C. This is indicated in Figure 4.14. Films grown at lower or higher temperatures show defect peaks. Defects are probably formed at these non-ideal temperatures, and nitrogen incorporation is decreased, as indicated by small DAP peaks.

Films grown with the aid of the laser exhibit spectra as shown in Figure 4.15. The PL shows a peak around 444 nm, and a dominant DAP peak centered around 460 nm with a smaller peak at 464 nm. The PL spectra does indicate films of good crystalline quality, since there are no defect peaks. Also, the strong DAP indicates nitrogen incorporation. But, C-V analysis shows that these films lack active electrical carriers. We can only postulate that this occurs because the annealing technique is not effective in activating these films.

PL spectra of films grown with direct above-gap illumination show characteristics as indicated in Figure 4.16. These films exhibit a broad DAP peak centered around 460 nm. The ABE and DBE peaks are of much smaller magnitude.
Figure 4.14: PL spectra dependence on growth temperature
Figure 4.15: PL spectra of films grown with laser
Figure 4.16: PL spectra of films grown with UV radiation
Comparision of PL spectra taken before and after anneals indicated an increase in the ratio of the magnitude of the 460.5 nm peak to the magnitude of the 465.5 nm peak. This is illustrated in Figure 4.17.

Figure 4.17: Comparision of PLs before and after anneal
4.13 Possible mechanisms

The chemical reactions occurring in ZnSe CVD processes are not yet well understood. Possible reactions could be:

\[(\text{CH}_3)_2\text{Zn} + \text{H}_2 = \text{Zn} + 2\text{CH}_4\]  \hspace{1cm} (4.1)

\[(\text{CH}_3)_2\text{Zn} = \text{Zn} + \text{C}_2\text{H}_6\]  \hspace{1cm} (4.2)

\[(\text{C}_2\text{H}_6)_2\text{Se} + \text{H}_2 = \text{Se} + 2\text{C}_2\text{H}_6\]  \hspace{1cm} (4.3)

Ammonia dissociation has been studied at elevated temperatures [43], but not much is known about how the NH\textsubscript{3} dissociates under our ZnSe MOCVD conditions. It has been established [44] that NH\textsubscript{3} dissociates mainly into NH\textsubscript{2} and NH. But, NH generation is suppressed in a H\textsubscript{2} atmosphere. Since hydrogen is our carrier gas, it is likely that the NH\textsubscript{3} dissociates predominantly into NH\textsubscript{2}, which might break down to yield N in a secondary reaction. The N may remain bonded to a H that occupies an interstitial space, resulting in passivation of the acceptor. That could be the reason why annealing is necessary to break the bond and activate the acceptor. Nitrogen incorporation possibly occurs by a different mechanism for the laser-assisted CVD films. The nitrogen seems to form a stronger bond with an interstitial atom, a bond that is not broken by annealing procedure. Hence, the films remain inactive electrically.
4.14 Summary of experiments

A series of experiments have been performed to determine the optimum parameters for growth of p doped ZnSe. Doping densities as high as $7.9 \times 10^{17}/\text{cm}^3$ have been achieved. The optimized conditions are as follows:

- Anneal Temperature: Greater than $300^\circ\text{C}$
- Growth Temperature: $475^\circ\text{C}$
- Mass Flow Rate of NH$_3$: 2 sccm
- Absence of laser or UV irradiation

These conditions yield ZnSe of doping density comparable to the best obtained by MBE.
Chapter 5

Conclusions and Recommendations

We have demonstrated a method of obtaining p doped ZnSe films. Experiments have been performed to optimize growth conditions. Using a MOCVD process, we have obtained p doped ZnSe having doping densities of as much as $7.9 \times 10^{17}$/cm$^3$. This is higher than any reliable previous reports of p doped ZnSe grown by MOCVD, and is comparable to the best results obtained by MBE techniques. As indicated in the first chapter, MBE is an expensive process and is not suited for production on a mass scale. Thus it is significant that we have been able to demonstrate growth of high quality p doped ZnSe using a MOCVD technique. MOCVD is a much cheaper process with a high throughput, and can be utilized for manufacture of chips in the real world.

The next step would be to develop a ZnSe pn junction, with the ultimate goal being the development of a ZnSe blue LED. We seem to be well in the range necessary for p ZnSe; the 3M group has demonstrated a rudimentary ZnSe LED using p doped ZnSe having carrier concentration of $3 \times 10^{17}$/cm$^3$. As indicated earlier, n type ZnSe is easy to obtain. So the next step would be to get a n dopant and proceed with the effort to develop a ZnSe LED.
Bibliography


