CHAPTER 2

GROWTH OF ZnSe, CdS AND CdIn$_2$S$_4$ SINGLE CRYSTALS AND THEORETICAL STUDIES ON OPTIMIZATION OF GROWTH CONDITION

2.1 GROWTH OF II-VI COMPOUNDS

2.1.1 Introduction

II-VI compound materials are the earliest materials used on a large industrial scale for the production of semiconductors. In the third decade of this century they became well known as "kristallphosphore" (crystal phosphors) and were used as cathode-ray tube screen materials (Hartmann et al 1982). These compounds cover a very broad range of electronic and optical properties due to the large variations in their energy band gaps between -0.3eV and 3.7eV. In recent years the II-VI compound semiconductors have attracted much attention for their technological importance appropriate for optoelectronic devices such as semiconductor diode lasers and light-emitting diodes (LEDs). A wide variety of methods have been applied to grow these materials in the form of bulk crystals or thin films with particular electrical and optical properties for suitable device applications. In this regard, enormous amount of work has been carried out to find the contribution of different factors in changing the physical properties of grown materials. Inspite of such extensive work there still remains several unanswered questions concerning the growth kinetics, structure, preparation and physics of these compounds.
2.1.2 Structure

All of the II-VI compounds MX (M=Zn,Cd;X=S,Se,Te) crystallize in either the zincblende or in the wurtzite structure (polymorphism). The energy differences between these two phases are small. Thus, faulting induced by phase transformations is a major problem of the compounds for which the stable phase is cubic at room temperature (Fitzpatrick 1988). The low stacking fault energy is as a result of higher ionicity of II-VI compounds. The softness of these materials makes them susceptible to strain, but, on the other hand, the rapid self-diffusion may lead to the easy relief of strain. The structures are based on the space group F\text{4}3m and P\text{6}3mc. Figures 2.1 and 2.2 show the arrangement of atoms in crystals of these compounds with cubic and hexagonal structures respectively (Roth 1967). In the zincblende as well as in the wurtzite structure, each M or X atom is tetrahedrally surrounded by four X or M atoms, respectively. In the zincblende structure there are 4MX per unit cell with the coordinates:

<table>
<thead>
<tr>
<th>1 1</th>
<th>1 1</th>
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<tbody>
<tr>
<td>0 0 0;</td>
<td>0 0</td>
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</table>

2 2 2 2 2 2

In the wurtzite arrangements there are two molecules in the hexagonal unit cell with 2M at

2 1 1

0 0 0, - - - and 2X at 0 0 u and - - ++u, with u = - .

3 3 2

3 3 3 8

2.1.3 Importance and applications

The specific properties of these compounds are their rather large ionicity leading to a relatively wide energy gap between the valence and
Figure 2.1 The arrangement of metal atoms (small filled circles) and non-metal atoms (large open circles) in zincblende, the cubic form of ZnS
Figure 2.2  The arrangement of metal atoms (small filled circles) and non-metal atoms (large open circles) in wurtzite, the hexagonal form of ZnS
conduction band, at least with lighter component elements, and the fact that their wide gaps are direct gaps, resulting in high optical transition probabilities for absorption and luminescence. From the same origin, higher ionicity, the effective masses of the carriers are substantially higher in the II-VI compounds than in the elemental and in the III-V compounds. In addition, the radiative lifetime is smaller because of the high dipole transition probabilities. Table 2.1 compares the above mentioned properties of II-VI compounds and those of some technologically important elemental and III-V compound semiconductors (Hartmann et al 1982).

Table 2.1

Comparison of technologically important semiconductors and II-VI compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy gap (eV)</th>
<th>Type of transition</th>
<th>Mobility (cm² V⁻¹ s⁻¹) (electron)</th>
<th>Effective mass</th>
<th>Ionicity</th>
<th>Lifetime (s) (electron)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.67</td>
<td>Indirect</td>
<td>4000</td>
<td>1.58,0.08</td>
<td>0</td>
<td>10⁻³</td>
</tr>
<tr>
<td>Si</td>
<td>1.11</td>
<td>Indirect</td>
<td>1500</td>
<td>0.91,0.19</td>
<td>0</td>
<td>10⁻³</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.43</td>
<td>Direct</td>
<td>9000</td>
<td>0.065</td>
<td>0.31</td>
<td>10⁻⁸</td>
</tr>
<tr>
<td>GaP</td>
<td>2.3</td>
<td>Indirect</td>
<td>180</td>
<td>0.35</td>
<td>0.33</td>
<td>10⁻⁷</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.73</td>
<td>Direct</td>
<td>650</td>
<td>0.13</td>
<td>0.70</td>
<td>≤ 10⁻⁹</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2.25</td>
<td>Direct</td>
<td>100</td>
<td>0.11</td>
<td>0.61</td>
<td>≤ 10⁻⁹</td>
</tr>
<tr>
<td>CdS</td>
<td>2.42</td>
<td>Direct</td>
<td>350</td>
<td>0.20</td>
<td>0.69</td>
<td>≤ 10⁻⁹</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.67</td>
<td>Direct</td>
<td>200</td>
<td>0.17</td>
<td>0.63</td>
<td>≤ 10⁻⁹</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.66</td>
<td>Direct</td>
<td>150</td>
<td>0.28</td>
<td>0.62</td>
<td>≤ 10⁻⁹</td>
</tr>
</tbody>
</table>

With respect to gap energies, mobilities and lifetimes, the technologically well developed elemental and III-V semiconductors Ge, Si, GaAs and GaP are obviously complemented by the wide gap II-VI compounds, CdS, ZnS, ZnSe and ZnO. To date, the material quality of II-VI semiconductors remains inferior to that of Si and III-V semiconductors. The
limitations in the microscopic and macroscopic material properties of II-VI compounds have led to a poor control of the electrical properties of II-VI semiconductors. Due to these limitations, II-VI materials have been primarily used as opto-electronic devices in spectral regions where Si and III-V devices cannot provide the required band gap. For example, ZnS, ZnSe, CdS and CdSe are excellent luminescent materials and they potentially offer devices in the visible spectral region. The resurgence in II-VI materials in the last several years has been triggered by the expectation that the current semiconductor technology developed for III-V compounds when applied to II-VI materials will result in better and novel devices. The application of wide band gap II-VI materials as semiconductor junction devices has been hampered by the problem encountered in making both conductivity n- and p-type materials from the same compound. To identify the role of various extrinsic impurities and intrinsic defects in optical and electrical properties in these II-VI compounds, emphasis has been placed in recent years on the growth of purer bulk crystals and epitaxial thin films at low temperatures (Bhargava 1988).

Because of new epitaxial growth techniques such as molecular beam epitaxy (MBE) and metalorganic chemical vapour deposition (MOCVD), there has been increasing interest in new II-VI device research during the past decade. These growth methods and advances in other preparation techniques permitted the growth of good quality heterojunction (HJ), quantum well (QW) and superlattice (SL) structures such as ZnTe-ZnSe SL (Frandon et al 1994), CdTe/CdS HJ (Simmons et al 1991), ZnSe/ZnMnSe QW (Schulzgen et al 1994) and many others. A review on the applications of II-VI compounds shows that these materials in the form of bulk single crystals or thin films are used in light emitters, detectors, linear and nonlinear optical devices, semiconductor electronics and other devices (Colak 1993).
Among II-VI compound materials, ZnSe has received greater attention because of its structure, and band gap which gives the promise of fabricating diode lasers and LEDs operating at blue colour range, and to date thin films of ZnSe have been grown on GaAs substrates whose lattice constant is close to ZnSe. Heteroepitaxial growth of ZnSe on GaAs has shown to be inconvenient due to problems such as misfit dislocations, diffusion of host atoms into the epitaxial layer and compressive stress in ZnSe (Ponce et al 1983; Williams et al 1984; Fujiwara et al 1986). To overcome difficulties of heteroepitaxial growth in the ZnSe-GaAs system, homoepitaxy has to be applied using ZnSe substrates. ZnSe single crystals grown by the iodine transport (Koyama et al 1988) have shown to be proper substrates with large twin free area, for homoepitaxial growth of this material by MOCVD (Yodo et al 1988). In recent years, a great amount of work has been carried out for study on the lasing properties of ZnSe-based semiconductors using optical pumping and electron beam pumping methods (Pessa and Ahn 1993). Room temperature lasing has been reported in optically pumped bulk ZnSe single crystals grown by the seeded physical vapour transport (SPVT) technique (Yang et al 1991). Waveguides have been made using heterojunction of ZnSe-ZnSSe single crystals with thickness of the order of micrometers grown on GaAs substrates by MOCVD method (Jupina et al 1992).

In the range of mass productions, because of low-absorption at infrared wavelengths as well as its visible transmission, ZnSe has been a preferred material for making lenses, windows, output couplers and beam expanders used in high power laser systems, thermal imaging and night vision.

In application of II-VI compounds in the area of detectors, CdS has received great interest due to its optical properties. During last years, it has been used as photoconductive (Svechniknov and Kaganovich 1980) and photovoltaic detectors (Livingstone et al 1978). One of the most suitable
applications of II-VI photovoltaic devices is solar-cells and there has been continuous interest in the heterojunctions such as CdTe/CdS. This heterojunction is formed by MOCVD growth of CdTe thin films on the substrates prepared from CdS single crystals grown from vapour (Simmons et al 1991; Russell et al 1985).

2.1.4 Theoretical studies on the optimization of growth condition for the growth of CdS single crystals

2.1.4.1 Importance of theoretical work

Single crystals of CdS have been grown at low temperatures by CVT technique but the establishment of the optimum growth condition has always been the major problem (Kaldis 1969; Matsumoto et al 1983). The exploratory work needed to achieve the desired results, when carried out in an empirical, trial and error fashion, will often be ineffective and time consuming. The slowness of the empirical approach arises from the many experimental variables which can affect the results, coupled to the time needed to set up and run an experiment before it can be evaluated. In general, the perfection of the crystal grown by vapour methods increases with the constancy of the flow of material which is carried out from the source zone to the deposition zone through different mechanisms such as diffusion, Stefan flow and convection and on the stability of the deposition zone temperature (Simanovskii 1969). Slight drop in temperature of the deposition zone during growth process causes multiplicity of crystal seeds which leads to intergrowths and change in composition of the gaseous mixture (Simanovskii 1970). Since the flow is very much temperature dependent and control of temperature at the growth interface is always poorer than the accuracy shown by temperature controllers in the furnace, i.e. ±0.1°C and temperature variation upto ±2°C has been observed along the quartz ampoule inside the double-zone horizontal furnace. Though proper change in other growth parameters such as concentration of the transporting agent makes it possible to reduce the effect of the temperature
on flow of the material. Furthermore to increase the size of the grown crystals, the primary nucleation should be controlled (Kaldis 1965). The primary nucleation depends on supersaturation and the transport rate and these two factors are the functions of zone temperatures and transporter concentration. This makes it necessary to determine how the composition of the vapour varies with temperature and with the initial transporter concentration (Faktor and Garrett 1974). A simple thermodynamical model has been introduced for the CdS-I$_2$ system which enables us to calculate the partial pressure of the different components inside the CdS-I$_2$ system through which the optimum growth temperature for growth of CdS single crystals by CVT can be deduced. In the present investigation, some of the growth parameters such as partial pressure of the different components, temperature condition and concentration of the transporting agent have been taken into account for the calculation of optimum growth parameters. But there are some other factors such as the mechanism of transport, growth rate, undercooling and deviation from stoichiometry that can affect the quality of the growing crystals in closed tube CVT process and they have not been taken into consideration in the present study (Bottcher and Hartmann 1995).

### 2.1.4.2 Estimation of optimum growth condition

A suitable thermodynamic model to describe the vapour phase chemical transport of CdS with iodine is a triple reaction system

\[
\begin{align*}
\text{CdS}_{(s)} + I_{2(g)} & \rightleftharpoons \text{CdI}_{2(g)} + 0.5 \text{S}_2(g) \tag{2.1} \\
\text{CdS}_{(s)} + I_{2(g)} & \rightleftharpoons \text{Cd}_{(g)} + 2I_{(g)} + 0.5 \text{S}_2(g) \tag{2.2} \\
\text{CdS}_{(s)} + 2I_{(g)} & \rightleftharpoons \text{CdI}_{2(g)} + 0.5 \text{S}_2(g) \tag{2.3}
\end{align*}
\]

neglecting the dissociation of the solid CdS via
\[
\text{CdS}_{(i)} \rightleftharpoons \text{Cd}_{(g)} + 0.5 \text{S}_{2(g)} \quad (2.4)
\]

or the dissociation of CdI\(_2\) vapour via

\[
\text{CdI}_{2(g)} \rightleftharpoons \text{Cd}_{(g)} + \text{I}_{2(g)} \quad (2.5)
\]

Also assuming that the diatomic sulphur molecules predominate, the thermodynamical model for CdS-I\(_2\) system can be described in the simplest form to a first approximation, assuming the vapour phase contains only the four components I, I\(_2\), S\(_2\) and CdI\(_2\), by reaction (2.1) along with the well-known reaction

\[
\text{I}_{2(g)} \rightleftharpoons 2\text{I}_{(g)} \quad (2.6)
\]

It has been shown that among the reactions (2.1), (2.2) and (2.3), the reaction (2.1) is more important for the transport of materials from source zone to deposition zone (Attolini et al 1990). Conservation of iodine inside the CdS-I\(_2\) system and assumption of the exact stoichiometry of CdS in source material give the following Equations

\[
n_{\text{I}_{2}} = [n_{\text{I}_{2}} + (1/2)n_{\text{I}} + n_{\text{CdI}_{2}}] \quad (2.7)
\]

\[

P_{\text{CdI}_{2}} = 2p_{\text{S}_{2}} \quad (2.8)
\]

respectively, where \(n_{\text{I}_{2}}\) is the number of moles of initial iodine and the other \(n\)'s are the numbers of moles of the corresponding components. The equilibrium constants for reactions (2.1) and (2.6) are given as

\[
k^{(1)} = \frac{p_{\text{CdS}} (p_{\text{S}_{2}})^{0.5}}{p_{\text{I}_{2}}} \quad (2.9)
\]

\[
k^{(6)} = \frac{(p_{\text{I}})^{0}}{p_{\text{I}_{2}}} \quad (2.10)
\]

Considering that iodine gas inside the closed ampoule behaves as an ideal gas, the Equations (2.7) to (2.10) will be resulted to
in which $M_i$ is the atomic weight of iodine, $c$ is initial concentration of iodine, $T$ is the temperature of the reactor and $R$ is universal gas constant.

The equilibrium constants for reactions (2.1) and (2.6), i.e. $k^{(1)}$ and $k^{(6)}$, as a function of temperature, are given by (Hartmann et al. 1982).

\[
\log k^{(1)} = 9.27 - 5444 T^{-1} - 4810 T^{-2} - 1.33 \log T - 3.15 \times 10^{-4} T
\]
\[
\log k^{(6)} = 4.34 - 7879T^{-1} + 4264 T^{-2} + 0.33 \log T + 2.0 \times 10^{-5} T
\]

The partial pressures of components inside the reactor may be calculated as a function of temperature ($T$) and the initial concentration of iodine ($c$) by numerically solving the Equation (2.11) for the range 500-1200°C in steps of 50°C, with transporter concentrations of 0.5-15 mg/cm$^3$ (in steps of 0.5 mg/cm$^3$).

Figure 2.3 shows the calculated partial pressures of $p_{t_1}$, $p_{t_2}$, $p_{S_2}$ and $p_{CdI_2}$ for $c=5$ mg/cm$^3$ as a function of temperature. The value of $\alpha=p_{CdI_2}/p_{t_2}$, where, $p_{t_2}=[p_{t_2}+(1/2)p_{i}+p_{CdI_2}]$ correlates the ratio between the number of the CdI$_2$ molecules and total iodine molecules in the gaseous phase inside the CdS-I$_2$ system. Figure 2.4 shows the variation of $\alpha$ as a function of temperature for various concentration of transporter for $T_2$-$T_1$=50°C. Figure 2.5 shows the numerical values of $\Delta\alpha=\alpha(T_2)-\alpha(T_1)$ as a function of deposition temperature ($T_1$) for various values of concentration of the transporter. Since there is no much difference between the values of $p_{t_2}$ in source and deposition zones for $\Delta T$=50°C, therefore $\Delta\alpha$ can be approximated to be equal to $\Delta p_{CdI_2}/p_{t_2}$. In addition, it has been shown that the change in transport rate is proportional to the $\Delta p_{CdI_2}$ i.e. the difference in partial pressure of CdI$_2$ in growth and deposition zones (Bottcher and Hartmann 1995). Though without considering the type of migration along the tube, as a first approximation it can be assumed that the transport rate is proportional to
Figure 2.3 Partial pressures $p_0$, $p_{I_2}$, $p_{S_2}$, and $p_{CdI_2}$ as a function of temperature for $c=5$ mg/cm$^3$ in CdS-I$_2$ system.
Figure 2.4 Variation of $\alpha$ with temperature for various concentrations of iodine
\( \Delta \alpha \), i.e. the number of moles of CdS transported in time \( t \) \((n_{\text{CdS}})\) is proportional to \( \Delta \alpha \times t \). As observed from the Figure 2.5, as the concentration of transporting agent increases the curves become more broadened and the position of the peaks shift to higher temperatures. For all the curves \( \Delta \alpha \) changes slowly at the temperatures nearer to the peak positions. This shows that for a particular amount of concentration of transporter there is an optimum growth temperature, and vice versa, for which the change in flow of material as well as its stability at the interface of the growing crystal is minimum. Selecting growth temperatures at the points nearer to the peaks in Figure 2.5 for every concentration of transporter reduces the sensitivity of the transport rate to the temperature fluctuations along the ampoule inside the furnace. Figure 2.6 shows the amount of change in transport when there is a fluctuation in temperature upto \( \pm 2^\circ\text{C} \) in CdS-I\(_2\) system for three different growth temperatures for \( \Delta T=50^\circ\text{C} \), \( c=5 \text{ mg/cm}^3 \) and ampoule geometry with dimensions \( l=20 \text{ cm}, d=1 \text{ cm} \) calculated following Mandel (1962) and Attolini et al. (1990). Figure 2.7 shows the partial supersaturation \( \Delta p_{\text{CdS}}/p_{\text{CdS}}(T_1) \), which is the ratio of the difference in \( p_{\text{CdS}} \) between the two zones to that in deposition zone, as function of \( T_1 \) for \( \Delta T=50^\circ\text{C} \) and various \( c \). It is shown that when the concentration of the transporter decreases, the supersaturation decreases so that the nucleation rate, which depends on supersaturation, decreases. For the growth of good quality large size single crystals, the optimum value of transporter concentration corresponding to a low supersaturation in the reactor should be used.

2.1.4.3 Growth of CdS single crystals

There has been a long standing interest in CdS because of its optical and electrical properties. Large band gap (-2.5 eV) and high quantum efficiency of CdS, means that it has uses ranging from being a window material for solar cells to colouring plastics (Sobiesierski et al 1990). Single crystals of CdS have been grown largely by vapour and in limited
Figure 2.5 Variation of $\Delta \alpha$ with deposition temperature $(T_o)$ for various concentration of iodine
Figure 2.6 The amount of change in transport rate when there is a fluctuation in temperature up to ±2°C in CdS-I₂ system for three different growth temperatures for ΔT=50°C, c=5 mg/cm³ and ampoule geometry with dimensions l=20 cm, d=1 cm
Figure 2.7 Change of relative supersaturation with deposition temperature ($T_i$) for various concentration of iodine
cases by melt (Medcalf and Fahrig 1958), solution and flux methods (Rubenstein 1968). Vapour growth of CdS at low temperatures was first achieved by Nitsche (1960) who utilized the chemical vapour technique with iodine as the transporting agent. The growth of CdS by CVT technique was continued by different researchers and crystals with different morphological habits and sizes were grown in different experimental conditions. Paorici (1969) reported the growth of CdS single crystals in the form of hollow prismatic rods in an iodine-rich atmosphere. Kaldis (1969) has extensively studied the growth of CdS single crystals by CVT in different experimental conditions such as source temperature \(750°C<T_2<1120°C\), undercooling \(5°C<ΔT<200°C\) and iodine concentration \(0.1mg/cm^3<c<12mg/cm^3\) in order to find the suitable condition for control on nucleation and improve the size of the grown crystals. It showed that using vertical pulling method with iodine transport, controlled nucleation was possible only at iodine concentration less than \(0.2\) mg/cm\(^3\) and critical undercooling less than \(15°C\). But applying these conditions resulted in the growth of crystals with much deficiency in cadmium element. It was also reported that the CdS grown in different experimental conditions were showing different morphological habits such as hexagonal platelets, hollow conical and pyramidal habits due to random nucleation and only by using seed and undercooling of \(5°C\) CdS crystals with dimensions up to \(10\) mm were grown. The change in morphology of CdS crystals with change in growth temperature and iodine concentrations was also reported by other researchers. Matsumoto et al (1983) observed that CdS crystals grown in different temperatures and different iodine concentrations showed different morphological habits such as needles, polyhedron, prisms, pyramids, rods, platelets, dendrites and irregular shapes. Attolini et al (1986) improved the perfection of CdS single crystals grown by CVT by adopting time-increasing supersaturation method which showed that small supersaturation does not exhibit skeletal and hollow forms. Later it was reported that using hydrogen as the transporting agent will improve the size of the CdS single crystals and also has several advantages such as better control of nucleation up to the point of obtaining
large crystals and lack of contamination of the grown crystals by transporting agent (Attolini et al. 1982). Paorici and Pelosi (1976) extensively studied the closed tube CVT mechanisms for the Cd:I\textsubscript{2} system from thermodynamical as well as hydrodynamical point of view and they calculated the mass transport rate as a function of overall pressure inside the tube considering the contribution of thermal convection, ordinary diffusion and Stefan flow in transport of material. Attolini et al. (1990) have applied the multireactional productivity function for predicting the maximum transport efficiency as well as some other CVT features such as the relative importance of the various chemical reactions and effect of inert gas on transport performance in the CdS:I\textsubscript{2} system.

The above survey shows that CdS crystals grown by CVT in closed tube using iodine as the transporting agent show different morphological habits and degree of perfection by change in experimental conditions such as growth temperature and iodine concentration. The growth temperature and iodine concentration have been changed in wide range to find empirically the most suitable growth condition which yields CdS crystals with better quality and bigger in size. However the growth temperature to be optimized for particular concentration of transporting agent which results in nearly perfect CdS single crystals remains yet to be found out. Hence the growth of CdS single crystals in different growth conditions have been studied to justify the agreement of theoretically predicted optimum conditions with experimental observations (Tafreshi et al. 1995).

2.1.4.4 Experimental details

The starting material was cadmium sulfide of spectroscopic grade (5 N purity). Before use, the powder was heat treated at 200-300 °C for several hours in vacuum. Three grams of heat treated powder was filled into a quartz ampoule, having length of 20cm and diameter of 1cm, along with iodine. Due to high vapour pressure of CdS, the ampoules were made from
quartz tubes having thickness of 2mm for safety reasons. The ampoule, cooled by ice, was evacuated to 2x10⁻⁵ torr and sealed off. The capsule was placed into the double-zone horizontal furnace controlled by Eurotherm controllers. A reverse temperature profile was developed across the ampoule over several hours to remove the sticking powder from the tip or deposition zone of the ampoule. The growth temperature \( T_g \) was varied from 600 to 950°C. The concentration of the transporter was varied from 1 to 10mg/cm³ and the difference in temperature of the source and deposition was kept constant \( \Delta T=50°C \) in all the growth runs. Each growth run was carried out for one week. After that, the furnace was cooled down to room temperature in 20 hours. The optical quality of the grown crystals was examined by optical transmission measurements in visible and NIR regions using spectrophotometer (HITACHI U 3400). Single crystallinity was confirmed by Laue photographs for the as-grown crystals.

2.1.4.5 Results and discussion

The crystals grown in different temperatures for the same amount of iodine concentration showed different habits and optical qualities. The crystals were orange, red and pale yellow in colour with the average dimensions of 3x2x1 mm³. The experimental results observed are in good agreement with the theoretical calculations. For instance, the following results have been obtained for the CdS single crystals which have been grown at three different temperatures (600, 750, 950°C) with 5 mg/cm³ concentration of the iodine and 50°C difference in temperatures of the source and growth. The crystals which have been grown at 750°C are having complete faces and their habits were mostly pyramidal and platelet. They were found to be more transparent compared to the CdS crystals grown in other temperatures for the same amount of transporter concentration. In general, the quality of the grown crystals was found to be good. This can be due to the stability of the flow of the materials which are transported from source zone to the growth zone and growth of crystals at the predicted
optimum growth temperature (750°C from Figure 2.5) corresponding to the 5mg/cm³ concentration of the iodine. The crystals which have been grown at 600°C (growth temperature), due to higher partial supersaturation, they are more number of smaller size crystals having needles and irregular habits and these crystals are poor in quality. The crystals which have been grown at 950°C were found to have poorly developed faces in most cases and showing less transparency. The deficiency in surface perfection and optical quality of the CdS crystals grown at 600°C and 950°C compared to the CdS crystals grown at 750°C, can be due to the variance of the transfer rate caused by small thermal fluctuation in temperature of the deposition zone where the slope of Δα curve is large. Due to temperature fluctuation, the temperature profile of the furnace will not have an uniform shape with respect to time. This instability in temperature profile leads to poor control on nucleation and affects the size of the crystal. In addition it alters the mass transport along the tube. By change in temperature, the contribution of different mechanisms such as diffusion and convection in mass transport will be changed with respect to time and hence the growing crystals have no definite morphology and regular habit.

Since the optical transmission measurements have been carried out for the crystalline samples having the same thickness (2mm) and equally polished surface, the difference in transmissions can be due to the scattering from defect centres. Because of the temperature fluctuation at the growth interface, defects such as precipitates, inclusions and dislocations may get into the lattice of the growing crystals and affect their optical quality. Figure 2.8 shows some of the CdS single crystals which have been grown at (a) 600°C, (b) 750°C and (c) 950°C for c = 5 mg/cm³ and ΔT=50°C. Figure 2.9 shows the Laue reflection from the basal plane of CdS single crystals grown at optimum growth temperature i.e.750°C.

The dislocation density of the CdS crystals grown at different temperatures was determined by etch pit measurements. The surface of the
as-grown CdS crystals parallel to the basal plane was etched with HNO₃+HCl and number of etch pits formed on the surface was counted under the visual field of Leitz optical microscope. The etch pit density (EPD) values were calculated in each area of 0.2x0.3 mm² based on the counted numbers. EPD values vary from 5x10³ cm⁻² to 5x10⁵ cm⁻². The etch pit density for the CdS crystals grown at 600°C, 750°C and 950°C were found to be 5x10⁵ cm⁻², 5x10³ cm⁻² and 10⁴ cm⁻² respectively. This is in agreement with the results of other studies which show that the CdS crystals grown at optimum growth condition have lower density of dislocations. These crystals are more suitable for substrate materials in making devices. Electrical properties of the as-grown CdS single crystals were determined by Hall effect measurements. The surface of the as-grown crystals was lapped and polished using diamond paste. Ohmic contacts were formed with In on the crystal surfaces. The surface of the sample was masked such that electrodes with same dimensions and equal distances were formed on the crystal. To achieve a better ohmic contact, crystals were annealed in inert atmosphere. All the crystals were found to be n-type conducting and they did not change their conductivity by annealing and quenching in the presence of sulfur vapour. The Hall effect measurements showed that the crystals have high resistivity. The carrier concentration of the CdS crystals was found to be 8.5x10¹⁶ cm⁻³.

2.1.5 Growth of ZnSe single crystals

Increasing attention has been focused on the growth of ZnSe single crystals for application as a substrate in blue light emitting diodes (Nishizawa et al 1985; Krasnov et al 1995). Growth of ZnSe single crystals has been initiated since 1958, but no report was mentioned on the size of the grown crystals in early literature. The first report on the growth of ZnSe single crystals with mentioning their size came from Nitsche (1960) who used CVT method for the growth of these crystals with the size of up to 4x4x3 mm³. Since 1960 there has been lot of report on the growth of ZnSe...
Figure 2.8 CdS crystals grown at (a) 600°C, (b) 750°C and (c) 950°C with $\Delta T = 50^\circ$C and $C = 5$ mg/cm$^2$
Figure 2.9 Laue reflection from the basal plane of CdS single crystals
single crystals mostly by vapour methods and in limited cases with other methods such as melt (Holton et al 1969; Rudolph et al 1994), solution (Unuma et al 1992) and solid state recrystallization (Woodbury and Hall 1967). The high melting point (1520°C), multi-twin patterns produced during phase transition from hexagonal to cubic at 1425°C and other defects produced at high temperatures have made growth of ZnSe from the melt difficult (Shone et al 1988). Attempts have been made by different researchers to grow ZnSe single crystals by CVT using iodine as transporting agent with bigger size and improved properties suitable for device applications (Bhargava 1988).

By using seed methods and applying lower undercooling (ΔT=7°C), ZnSe single crystals with dimensions of 20x15x15 mm³ were grown (Kaldis 1965). Later it was shown that grain size of the grown crystals depends strongly upon the undercooling and growth ampoule geometry and growth of ZnSe with dimensions of 24x14x14 mm³ with undercooling as low as 7°C using an ampoule with a steep conical tip was reported (Fujita et al 1979). Later there has not been any more improvement in size of the ZnSe single crystals grown by CVT and attempts have been oriented towards the growth of these crystals with more attention to their morphological perfection and improved electrical and optical properties. Kaldis (1974) has discussed that the morphology of the crystals grown from vapour phase depends on the mechanism which is a rate determining step. By changing the experimental conditions such as pressure, temperature and supersaturation, there will be an interplay between the mass transport, kinetics of the chemical reaction and/or surface reactions on the growth interface and one of these processes will become the rate determining step. Very recently it has been shown that change in experimental variables such as system pressure, temperature conditions and concentration of the transporting agent will affect the contribution of mass transport through the convection and diffusion mechanisms and affect the crystallographic perfection and morphological stability of the ZnSe single crystals grown by CVT method (Bottcher and
The growth aspect ZnSe single crystals by CVT has been studied with special emphasis placed on the formation of different micromorphological patterns formed on the surface of the crystals grown in different experimental conditions (Tafreshi et al. 1995a).

2.1.5.1 Experimental details

The pre-treatment of starting material for growth process was carried out by mixing a stoichiometric ratio of Zn and Se elements with 5 N purity and loading in quartz ampoule. The mixture was heated in vacuum at temperature of 850°C for 10 hours in order to remove volatile impurities and get homogenized polycrystalline of ZnSe. The formation of ZnSe was verified by taking X-ray diffractogram. Ampoules with the length of 23 cm and diameter of 1 cm were filled with 3 grams of heat-treated ZnSe polycrystalline powder along with iodine at a concentration of 3 mg/cm³ of the empty space of the ampoule. The ampoules, cooled by ice, were evacuated to 2x10⁻⁶ torr and sealed off. The capsules were placed into double-zone horizontal furnace controlled by Eurotherm controllers with the accuracy of ±0.1°C. PID controllers with the accuracy of ±5°C were also used in one of the growth runs. A reverse temperature profile was developed across the ampoule with growth zone in higher temperature for 24 hours to remove the sticking powders from deposition zone of the ampoule and diminish the active sites. Different growth runs were carried out for different undercooling (ΔT) values using same composition of starting materials and ampoule geometry keeping temperature of growth zone constant at 890°C. Each growth run was carried out for a week. At the end of each growth process, the furnace was slowly cooled to room temperature at a cooling rate of 50°C/hr to prevent thermal strains. The structure and morphology of the grown crystals were studied using computer aided single crystal X-ray diffractometer (Make: ENRAF MONIUS, FR 590) attached with rotating goniometer. The composition of the grown crystals was examined by AAS measurements. The microscopic observation of the as-grown crystal surfaces
was carried out using optical microscope and SEM. Gold coating was made on all the samples before they were analyzed by SEM.

### 2.1.5.2 Morphological and structural studies

Many individual crystals of different sizes were observed at the deposition zone of the ampoules in all the growth runs. The crystals observed at the tip of the ampoule were smaller in size compared to those grown far from the tip position. Intergrowths were observed mostly in the case of growth runs when the furnace was controlled by PID controllers in both zones. The crystals grown with lower undercooling were light brown and the crystals grown with higher undercooling were yellowish brown in colour. The habit and average dimension of the grown ZnSe crystals along with applied growth conditions have been summarized in Table 2.2. Most of the growth runs resulted in the growth of ZnSe with cubic structures. Single crystals of ZnSe with hexagonal structures were also observed in one of the growth runs. X-ray analysis showed that the cubic ZnSe single crystals are having large (111) and small (110) and (211) faces and lattice parameter of these crystals is $a=5.6649 \, \text{Å}$ which is in good agreement with ASTM reported values i.e. $a=5.669 \, \text{Å}$. The result of AAS measurements of the grown crystals with cubic structures showed that there is slight deviation in stoichiometry due to the deficiency of the zinc atoms. It has been reported that the presence of excess chalcogen in the gas phase facilitates the formation of cubic phase (Simanovski 1975). As-grown ZnSe crystals showed n-type conductivity after annealing in Zn vapour at 1070°C for 140 hours. The carrier density for annealed crystals was found to be $5 \times 10^{17} \, \text{cm}^{-3}$ by Hall effect measurements. The etch pit density of the as-grown crystals was measured to be $5 \times 10^{4} \, \text{cm}^{-2}$. Figure 2.10 shows the cubic ZnSe single crystal with (111) upper face. The layers grown in the form of triangles are showing the three fold symmetry of the (111) face. Figure 2.11 shows the ZnSe single crystal with hexagonal structure and more developed (001) face.
Figure 2.10  Cubic ZnSe single crystal with (111) upper face

Figure 2.11  Hexagonal ZnSe single crystal

Figure 2.12  Microsteps on ZnSe crystals grown with lower undercooling

Figure 2.13  Kinks with well resolved structure grown with higher undercooling
Table 2.2
Crystal habit and microstructural patterns observed for ZnSe crystals

<table>
<thead>
<tr>
<th>No. of growth runs carried out</th>
<th>Undercooling ((\Delta T^\circ C))</th>
<th>Crystal habit &amp; dimensions ((mm^3))</th>
<th>Microstructures observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>15</td>
<td>Cubic platelets and pyramidal 2x3x1</td>
<td>Microsteps</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>Cubic, tetragonal and hexagonal platelets 2x3x0.2</td>
<td>Kinks &amp; Microsteps</td>
</tr>
<tr>
<td>1*</td>
<td>60</td>
<td>Thin platelets 2x3x0.2</td>
<td>Spirals &amp; Bunch of steps</td>
</tr>
</tbody>
</table>

* Poor control on temperature at growth interface due to PID controllers.

2.1.5.3 Micromorphological studies

The microscopic observation of surface of the as-grown crystals showed the formation of different microstructural patterns such as microsteps, spirals and kinks. Table 2.2 shows the different types of microstructures which have been observed in each growth condition. In addition to the microstructural patterns, it was observed that the surface of the as-grown crystals have been covered by fine crystals and flecks left by the transporting agent. Removing these particles which have been attached to the surface by chemical agents can damage the microstructural features on the crystal surfaces.

The crystals grown with lower undercooling \((\Delta T=15 \, ^\circ C)\) showed mostly smooth and flat faces without microstructures up to a SEM magnification of 3000X. Microsteps were also observed on surface of some
of the crystalline pieces. Figure 2.12 shows microsteps on the surface of the ZnSe crystals grown with lower undercooling. Microsteps are in the form of parallel and straight lines with the thickness of the order of micrometer. Steps have not distributed uniformly on the surface and they are appearing to be more dense and bunched in some of the surface portions. This can be due to the nonuniformity in the supersaturation caused by slight local thermal fluctuation on the surface of the crystal during growth process. Two following mechanisms have been suggested for the generation of these microsteps (Nakada and Bauser 1989). They can be generated at the emergence points of dislocations and expanded over the surface. In addition to dislocations, crystal edges and corners frequently favour the nucleation of new layers and therefore are able to spontaneously generate microsteps. Since no sign of screw dislocation is observed on the surface of the crystal shown in Figure 2.12 and moreover the microscopic observation showed that the microsteps are continued on the surface upto the surface edges, it is more probable that microsteps are originating from crystal edges. The surface of the crystals grown in higher undercooling condition (ΔT=60°C) showed to be rough compared to the surface of the crystals grown with lower undercooling (ΔT=15°C). Thermodynamical analysis of the ZnSe-I₂ system has shown that for a particular concentration of iodine, by increase in the undercooling value, Δp_{Znl₂} or difference in partial pressure of Znl₂ in source and growth zones increases (Simanovskii 1969). Though, the contribution of mass transport through convective process is more and it is resulted in instability at the growth interface and formation of crystal surfaces with more density of steps (Bottcher and Hartmann 1995). Figures 2.13, 2.14 and 2.15 show different type of features observed on the surface of the crystals grown with higher undercooling. Figure 2.13 shows the kinks with well resolved structure. It is difficult to resolve them under an optical microscope since the separation is very small. Figure 2.14 shows the similar structure which has been formed on rough surface of the grown crystals. Figure 2.15 shows the formation of microsteps with irregular shapes formed between two flat faces.
Figure 2.14 Kinks observed on the rough surface of the ZnSe single crystals grown with higher undercooling.

Figure 2.15 Steps with irregular shapes on the surface of the ZnSe single crystals grown with higher undercooling.

Figure 2.16 Bunching of spiral steps grown with instability at the growth interface.

Figure 2.17 Microstructure showing unusual combination of fundamental morphological features.
The surface of the crystals grown with higher undercooling value (ΔT=60°C) and poor control on temperature of the growth zone showed spirals (Figure 2.16) and structures with bunch of steps (Figure 2.17). Oscillation of the temperature at the growth zone causes instability in flow of the material arriving to the growth interface. Hence it leads to the formation of microstructures with incomplete faces. Figure 2.16 shows part of the spirals with different thickness which have grown under this condition which is consistent with Hottenhuis and Lucasius (1986) report. Figure 2.17 is an unusual combination of two fundamental morphological features which are separately treated by the main theories of crystal growth: train and bunches of steps (BCF theory, two dimensional nucleation) and wave like morphological perturbations (morphological stability theory). The active coexistence of these features has been confirmed in several micrograph of crystals growing at high temperatures from the vapour. Similar features have been observed on rare earth phosphides which have been grown at high temperatures (T~2100°C) from the vapour (Kaldis 1974). The present observation shows that these type of structures can also be formed on the surface of the crystals which are grown at low temperatures by chemical vapor transport technique. In summary, microscopic analysis showed that, the crystal surfaces were becoming rough with more density of kinks as the degree of undercooling increases. The results also showed that the instability of the growth interface will result in the formation of structures with bunch of steps.

2.2 GROWTH OF CdIn₂S₄ SINGLE CRYSTALS

Constant attention has been devoted to compounds of the chalcopyrite $A^+B^{III}C^{VI}_2$ or defect chalcopyrite $A^{II}B^{III}_2C^{VI}_4$ family due to their interesting nonlinear optical properties (Attolini et al 1992). The ternary compound CdIn₂S₄ is of potential interest both from a fundamental and practical point of view because of its structural, optical, electronic, and photoelectronic properties (Serpi et al 1986). CdIn₂S₄ is a photoconductive
semiconductor and belongs to the spinel family of the type $AB_2X_4$. The space group of spinel is $O_h^*$ ($Fd\bar{3}m$) where the A-sites are occupied by the divalent cations (Cd) and the B-sites by the trivalent cations (In) (Kambas et al 1985). Greenwood (1968) lists $\text{CdIn}_2\text{S}_4$ as a normal spinel which means that Cd atoms occupy tetrahedral sites and In atoms octahedral only.

II-III$_2$-VI$_4$ semiconductor compounds where II is Zn, Cd or Hg; III is Al, Ga or In and VI is S, Se or Te were first grown 40 years ago by Hahn et al (1955).

The following methods have been used for the growth of II-III$_2$-VI$_4$ compounds (Radautsan et al 1984).

i) The fusion of A, B and C components (FC) or that of binary II-VI and III$_2$-VI$_3$ compounds (FBC)

ii) The chemical vapour transport (CVT)

iii) Growth from the melt (GM)

iv) The zone melting (ZM)

By means of FC and FBC, II-III$_2$-VI$_4$ compounds have been obtained in a polycrystal form. For growing big single crystals GM and ZM are being broadly used and by applying these methods single crystals of $15\times15\times60$ mm$^3$ sizes have been successfully grown. But there are practical difficulties involved in growing most of these materials by melt techniques and production of small samples almost always depends upon available vapour-phase (VP) chemical transport reactions (usually "iodine" transport) in closed tubes. The growth of $\text{CdIn}_2\text{S}_4$ single crystals by using CVT technique was first reported by Nitsche (Nitsche 1960). He obtained single crystals of $\text{CdIn}_2\text{S}_4$ with octahedra shape and $4\times4\times4$ mm$^3$ sizes using iodine as the transporting agent. Later the size of the $\text{CdIn}_2\text{S}_4$ single crystals grown by CVT was improved by adopting Time-varying temperature profile
method and crystals with dimensions of 8x10x12 mm$^3$ were obtained (Paorici et al 1982).

2.2.1 Experimental details

The starting material for the growth of CdIn$_2$S$_4$ was prepared by the following procedure. First polycrystals of In$_2$S$_3$ were prepared from In and S elements with 5N purity baked at 600°C in vacuum. Then the polycrystals of In$_2$S$_3$ were mixed with CdS polycrystalline powder and the mixture was heated in vacuum at 700°C. The polycrystalline synthesized powder of CdIn$_2$S$_4$ of 3 g together with 5 mg/cm$^3$ of 5 N purity iodine was filled into the quartz ampoule of length 20 cm and diameter 1 cm. The ampoule, cooled by ice, was evacuated to 10$^{-6}$ torr, and sealed off. The capsule was placed into a double-zone horizontal furnace controlled by using Eurotherm controllers. A reverse temperature profile was developed across the ampoule over several hours to remove the sticking chemicals from the tip or deposition zone of the ampoule and diminish the active sites. The source and growth zone temperatures were kept constant at 830°C and 780°C, respectively, throughout the growth run. The growth process was going on for one week. After that, the furnace was cooled down to room temperature in 20 hours.

Octahedrally shaped crystals with sharp edges were formed at the colder tip of the ampoule (Tafreshi et al 1995b). The grown crystals were light and blackish red in colour and they had some of the natural facets of good optical quality. The lattice parameters and morphology of the grown crystals were determined by single crystal X-ray diffraction measurements. Results showed that the grown single crystals are combination of (111) and (100) faces and cell parameter was a=10.850 Å which agrees with those reported in the literature (Watanabe et al 1986). Figures 2.18 and 2.19 show the X-ray powder diffractogram and XPS spectrum for the grown crystals respectively.
Figure 2.18: X-ray diffraction pattern of CdIn$_2$S$_4$. Intensity (a.u.)

2θ (degrees)

Intensity (a.u.)

20

40

60

220

400

422

511

533

444

311

440
Figure 2.19 XPS spectrum of CdIn$_2$S$_4$.  

- S$_2$p
- C$_{1s}$
- Ag 3d
- Cd 3d
- In 3d
2.3 CONCLUSIONS

In the present study, the following conclusions are drawn:

i) Optimum temperature was determined for the growth of CdS crystals by CVT technique for different concentration of transporting agent by calculating the partial pressure of different components inside the CVT reactor.

ii) Crystals of CdS were grown in temperature range of 600-950°C with change in iodine concentration from 1 to 10 mg/cm³. Grown crystal showed average sizes of 2x3x2 mm³ and different morphological habits such as pyramidal, hexagonal, needles and irregular shapes.

iii) For 5 mg/cm³ concentration of transporting agent, CdS crystals grown at theoretically predicted optimum growth temperature (750°C) showed more surface perfection and better optical quality compared to the crystals grown at different temperatures (600°C and 950°C) for the undercooling of 50°C.

iv) Single crystals of ZnSe were grown at 890°C with different undercooling values namely 15°C and 60°C and different control of temperature at the growth zone for undercooling of 60°C. The grown crystals are in the size of 2x3x2 mm³ having both cubic and hexagonal structure and different micromorphological patterns such as microsteps, spirals and kinks. Surface of the grown crystals showed tendency to become rougher with increase in undercooling.

v) Single crystals of CdIn₂S₄ with average size of 2x2x3 mm³ in octahedral morphology were grown by CVT techniques. Crystals are having good optical quality faces which are suitable for optical measurements.