CHAPTER 2

PREPARATION AND CHARACTERIZATION OF NANOPARTICLES OF CADMIUM SULPHIDE AND NANOSTRUCTURED CADMIUM SULPHIDE THIN FILMS

2.1 INTRODUCTION

The fabrication of conventional devices relies on the assembly of macroscopic building blocks with specific configurations. The shapes of these components are carved out of larger materials by exploiting physical methods. This top-down approach to engineered building blocks is extremely powerful and can deliver effectively and reproducibly microscaled objects. This strategy becomes increasingly challenging, however, as the dimensions of the target structures approach the nanoscale. Nature efficiently builds nanostructures by relying on chemical approaches. Tiny molecular building blocks are assembled with a remarkable degree of structural control in a variety of nanoscaled materials with defined shapes, properties, and functions. In contrast to the top-down physical methods, small components are connected to produce larger objects in these bottom-up chemical strategies. It is becoming apparent that the limitations of the top-down approach to artificial nanostructures can be overcome by mimicking nature’s bottom-up processes. Modern chemical synthesis has evolved considerably over the past few decades.¹ Now, experimental procedures to join molecular components with structural control at the nanometer level are available. A multitude of synthetic schemes to encourage the formation of chemical bonds between selected atoms in reacting molecules have been developed. Furthermore, the tremendous progress of crystallographic and spectroscopic techniques has provided efficient and reliable tools to probe directly the structural features of artificial inorganic and organic
compounds. It follows that designed molecules with engineered shapes and dimensions can be now synthesized in a laboratory relying on the tricks of chemical synthesis methods and the power of crystallographic and spectroscopic analyses.

Recently, semiconductor nanocrystals have attracted considerable interest because they exhibit strongly size dependent optical and electrical properties and these behaviors open new applications including high performance opto-electronic devices. The most studied nanocrystalline semiconductors belong to the II-VI group as they can be synthesized relatively easily as colloidal particulates or in thin film form. Among the II-VI compounds, CdS is one of the most studied material, as it has several applications such as photoconductors, laser materials, homo-junction and hetero-junction solar cell materials.

Different physical and chemical synthesis routes were adopted by different workers for the preparation of nanostructures of compound semiconductors especially cadmium sulphide nanoparticles. Even the shortest history of preparation of II-VI semiconductor nanoparticles has to start with the work by Henglein in 1982. Another milestone in the preparation of II-VI semiconductor nanocrystals is the work of Murray, Norris and Bawendi in 1993. Their synthesis is based on the pyrolysis of organo-metallic reagents like dimethyl cadmium and trioctyl phosphine selenide after injection into a hot co-ordinating solvent. This approach provides temporarily discrete nucleation and permits a controlled growth of nanocrystals. It is evident that within about a decade tremendous progress was made in the preparation of such systems. To illustrate what happened during this period of time, a few endeavors in both preparation and characterization from a number of different laboratories will be mentioned. Rossetti et al. reported on quantum size effects in the redox potentials and electronic spectra of CdS nanocrystals. The size distribution was studied using transmission electron microscopy (TEM), and the crystallinity and crystal structure were determined. In a series of publications, Henglein and co-workers placed stress on the dissolution of CdS particles and enlarged the field by the preparation of ZnS and ZnS/CdS co-colloids. Ramsden and Grazel presented the synthesis of CdS particles formed in aqueous solution from Cd (NO₃)₂ and H₂S or Na₂S. In 1985 Nozik appeared on the scene with a paper on phosphate-stabilized CdS and PbS colloids. A very large number of articles were published by Brus in the field of semiconductor clusters, from both experimental and
theoretical viewpoints. In 1986, fractional separation by exclusion chromatography of as-prepared sol of hexametaphosphate (HMP)-stabilized CdS particles was introduced, together with stopped-flow experiments on extremely small clusters. New preparative approaches were developed for the preparation of CdS particles in dihexadecyl phosphate (DHP) surfactant vesicles and the synthesis of colloidal CdSe, which has now become the most important model system for the preparation of nanoparticles. CdS sols with particles ranging in size between 4 and 6 nm were prepared by first precipitating Cd\(^{2+}\) ions with the stoichiometric amount of injected H\(_2\)S followed by an "activation" of the colloid by addition of NaOH and excess Cd\(^{2+}\) ions.

The importance of developing new synthetic procedures for preparing II-VI semiconductor nanoparticles was evident as, in 1993, a special issue of the Israel Journal of Chemistry was devoted to quantum size particles which contained several articles on the synthesis and characterization of II-VI semiconductor nanoparticles.33-36 Narrow size distribution of polydisperse CdS colloids were prepared by Matsumota et al. using selective photo corrosion. In order to replace the hazardous metal alkyls in the organometallic syntheses, a single source approach to synthesize II-VI nanocrystallites was presented by Trinidad and O'Brien.38

There are a number of reports on the properties of CdS in polycrystalline thick/thin film form prepared by various techniques such as spray pyrolysis, electrodeposition, molecular beam epitaxy, chemical vapor deposition, High pressure magnetron sputtering, metal organic chemical vapor deposition, and chemical bath deposition. However, the basic problem with CdS film is obtaining uniformity and stoichiometry of the film over a large area. The chemical bath technique is a relatively simple and inexpensive method to prepare homogeneous films with controlled composition. However, depending on the deposition conditions such as pH of the solution, temperature, stirring speed, and time of deposition, the quality as well as the stoichiometry of the films and hence their structural and optical properties differ.51

An effective way to obtain CdS films with desired properties is to introduce dopants. Ion implantation is potentially attractive as an alternative to chemical doping technique. Ion implantation into compound semiconductors has been investigated with
increasing frequency in recent years. It is a key technology for the fabrication of doped layers in semiconductor microelectronic devices, which has several advantages over the conventional doping technique such as reproducibility, good dopant profile control and uniformity. An important aspect of the application of implantation to semiconductor technology, in contrast to other processes, is that the number of implanted ions is controlled by the external system, rather than by the physical properties of the substrate. During ion implantation, the lattice damage produced by the energetic ions, significantly alters the electrical and optical properties of the material. Several reports are available on the studies of ion implanted CdS films prepared by different techniques.\textsuperscript{56-63}

The present chapter explains the preparation of CdS nanoparticles of two different grain sizes using controlled chemical route and the preparation of nanostructured CdS thin film using chemical bath deposition technique under various experimental conditions, and their structural and morphological characterization using different probing tools. The characterization of the samples was carried out by X-ray diffraction (XRD), thermo gravimetric analysis (TGA), high resolution transmission electron microscopy (HRTEM), high resolution scanning electron microscopy (HRSEM), and Rutherford back scattering (RBS). The effects of thermal annealing of the samples are also studied using XRD.

2.2 SYNTHESIS OF NANOPARTICLES OF CdS

Nanoparticles of CdS of two different grain sizes were prepared by controlled chemical precipitation technique. Two chemical routes were used in the present study. All the chemicals used were of analytical grade.

Method-1: 1M aqueous solution of cadmium acetate was prepared by dissolving 2.66gm of cadmium acetate \([\text{CH}_3\text{COO}]_2\text{Cd} \cdot 2\text{H}_2\text{O}\) in 10 ml of distilled water. 0.78 gm of Na\(_2\)S.12H\(_2\)O flakes was dissolved in 10 ml of distilled water for getting 1 M Na\(_2\)S aqueous solution. The above two solutions were dropped simultaneously and slowly with 80 ml of distilled water kept stirred vigorously for 1 hr at room temperature. 10 ml of 0.1 molar EDTA was used as the stabilizer. The precipitate was centrifuged and washed several times.
in distilled water and finally in acetone. The CdS powder obtained (sample code: C₁) was dried in a furnace at 80°C.

Method-2: 40 ml of 1 M cadmium acetate aqueous solution, 20 ml of 13 M ammonia solution, 10 ml of 7.2 M triethanol amine (TEA) \[ N(CH₂−CH₂OH)₃ \] and 100 ml of distilled water were mixed slowly at room temperature with vigorous stirring. 40 ml of 2 M thiourea solution was added to the above mixed solution at 85°C. Ammonia acted as the complexing agent and thiourea as the source of sulphur. The precipitate obtained was centrifuged and washed several times in distilled water and finally in acetone, and then dried at a temperature of 80°C in furnace (sample code: S₁). The samples C₁ and S₁ were then annealed at different temperatures between 200 and 500°C (Table 1) to study the heat induced transitions.

Table 1. Sample codes for nanoparticles of CdS.

<table>
<thead>
<tr>
<th>CdS nanoparticles prepared by method - 1</th>
<th>CdS nanoparticles prepared by method - 2</th>
</tr>
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<tbody>
<tr>
<td>Sample codes</td>
<td>Annealing temperature (°C)</td>
</tr>
<tr>
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<td>as-prepared</td>
</tr>
<tr>
<td>C₂</td>
<td>200</td>
</tr>
<tr>
<td>C₃</td>
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</tr>
<tr>
<td>C₆</td>
<td>400</td>
</tr>
<tr>
<td>C₇</td>
<td>500</td>
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</tbody>
</table>

2.3 PREPARATION OF NANOSTRUCTURED CdS THIN FILMS

Nanostructured CdS thin films were deposited onto glass substrates by chemical bath deposition technique. The substrate was first cleaned in nitric acid, followed by repeated washing in distilled water, and finally in acetone under ultrasonication. For the preparation of CdS films, 10 ml of 7.2 M triethanol amine was mixed with 100 ml of
distilled water and this mixture was stirred well. 40 ml of cadmium acetate aqueous solution and 20 ml of 13 M ammonia solution were dropped slowly into the mixture at room temperature. A cleaned glass substrate was mounted vertically in the beaker containing the mixed solution. 40 ml of 2 M thiourea solution was then added to the beaker containing the substrate at 85°C. After 25 minutes, the substrate was retrieved from the solution, washed with distilled water to remove loosely bound particles, and finally cleaned ultrasonically in distilled water. It was observed that CdS film obtained was yellowish, homogeneous, hard and specularly reflecting with very good adherence to the glass substrate (sample code: CT1). Following the same method, one more sample was prepared for time of deposition of 15 minutes (sample code: CT2). In the above method, ammonia acted as a complexing agent and thiourea as the source of sulphur. The mechanism of CdS film formation may be assumed to be controlled by the adsorption reaction of Cd\(^{2+}\) from Cd\((\text{NH}_3\)\(^4\)\(^{+}\)) and \(S^2-\) from the hydrolysis of thiourea as per the following reaction

\[
\text{Cd}\left(\text{NH}_3\right)^4\(^{+}\) + SC\left(\text{NH}_2\right)^2_2 + 2OH^- \rightarrow \text{CdS} + CH_2H_2 + 4NH_3 + 2H_2O \tag{1}
\]

The reaction scheme commonly accepted is shown below.

\[
\text{SC}\left(\text{NH}_2\right)^2_2 + 2OH^- \rightarrow S^{2-} + CN_H_2 + 2H_2O \tag{2}
\]

\[
\text{Cd}\left(L\right)^{2+} \rightarrow \text{Cd}^{2+} + nL \tag{3}
\]

\[
\text{Cd}^{2+} + S^{2-} \rightarrow \text{CdS} \tag{4}
\]

Sulphide ions are released in step 2 by hydrolysis of thiourea in the basic solution and Cd\(^{2+}\) ions are released by decomposition of reaction (3), L representing ligand species. When the ionic product exceeds the solubility product of CdS \(10^{-25}\) it precipitates (reaction 4) either in the bulk of the solution with the formation of colloids or at the surface of the substrate leading to the formation of a film. Consequently the film can be formed by two different mechanisms, the sedimentation of colloids or the direct reaction of elementary species at the surface (reactions 4) called the ion-by-ion process but better represented by the more general atom-by-atom denomination. Ion implantation were carried out on the nanostructured CdS thin film for various fluences from \(10^{14}\) to \(10^{16}\) ions/cm\(^2\) using low energy accelerator at IGCAR, Kalppakam. The beam current was maintained at 0.5 micro ampere. A vacuum of 3.2*10\(^{-6}\) torr was maintained inside the sample chamber. The implanted CdS thin film samples were annealed in vacuum at 350°C for 2 hrs.
Fig. 1. XRD patterns of as-synthesized nanoparticles of CdS (a) sample C₁ and (b) sample S₁
2.4.1 X-RAY DIFFRACTION (XRD) STUDY OF NANOPARTICLES OF CdS

For structural characterization, X-ray diffraction patterns of the samples were recorded using Philips Xperto Diffractometer with CuKα radiation (λ=1.5418 Å) over the diffraction angle, 2θ, between 20 and 60°. Figures 1 (a) and (b) present the XRD pattern of the nanoparticles of CdS prepared by two methods (C₁ and S₁).

The as-synthesized samples (C₁ and S₁) were predominantly of cubic phase as evident from the characteristic (111), (220) and (311) peaks. However, the weak shoulders observed in the XRD pattern of the sample S₁ corresponding to (110) and (101) peaks of hexagonal phase suggests the presence of small fraction of wurtzite phase. The diffraction peaks appear broad indicating small grain size of the as-grown samples. For the as grown samples, 2θ values of diffraction peaks observed at 26.9, 44, and 52° correspond to reflections from (111), (220), and (311) planes of cubic(zinc blend) CdS. Chalcogenides generally adopt the hexagonal (wurtzite) or cubic (zinc blend) structure, showing a diffraction peak for the hexagonal CdS phase also at 26.9°, corresponding to the (002) plane, which causes ambiguity. This result is a consequence of the coincidence of the interplanar distance for both phases in these respective directions. However, a peak at 28.33° which should be absent in the XRD pattern of cubic CdS phase, but should appear as the most intense peak for hexagonal CdS, was not observed for the as-grown samples, leading to the conclusion that the as-grown CdS samples were predominantly of cubic phase. The fractions of hexagonal phase in the samples were estimated from the total integrated intensities of (100), (103) and (002), (110) peaks. It may be noted that the (100) and (103) lines are unique to the hexagonal phase; while (002) and (110) peaks of hexagonal phase have the same 2θ values as those of the (111) and (220) peaks of cubic phase, respectively. The relative contents of hexagonal phase was calculated from the ratio \( \frac{I_{100}+I_{103}}{I_{002}+I_{110}} \). The relative content of the hexagonal phase in the samples C₁ and S₁ were estimated to be 15% and 20%, respectively.

The grain size of the nanoparticles of CdS were calculated from the Debye-Scherrer formula, \( D = \frac{K \lambda}{\beta \cos \theta} \) where D is the grain size, K is the shape factor which lies between 0.94 and 1.15 depending on the shape of the grains (K=1 for spherical crystallites),
Figure 2. Hall and Williamson plot for nanoparticles of CdS. (a) for sample C₁ and (b) for sample S₁.
\( \beta \) is the full width at half maximum (FWHM) of the diffraction peak in radians, \( \theta \) is the Bragg angle of the diffraction peak and \( \lambda \) is the wavelength of X-rays.\textsuperscript{13,66-68} Using the above equation, the approximate grain sizes for the samples C\(_1\) and S\(_1\) are found to be 1.8 and 2.9 nm, respectively.

It may be noted that in the discussion of Scherrer equation, it is assumed that the line breadth \( \beta \) arises only due to the small size of the crystallite. However, there can be another important contribution to the line broadening called the strain broadening of the diffraction peaks, which must also be taken into account for unambiguous determination of crystallite size. The strain may arise from a number of factors such as lattice defects, presence of impurities, large surface energy, thermal history, etc.\textsuperscript{69-73} In the context of nanocrystalline materials, micro-strain arises primarily from the large surface energy associated with the large surface to volume ratio of the samples.\textsuperscript{72,73} There are a number of established analytical methods for determining contribution to the line broadening due to micro-strain. Hall-Williamson method, Warren-Averbach method, single line method, Rietveld analysis, etc are some of the most successful methods for the purpose.\textsuperscript{69-73} Of these, Hall-Williamson approach is the simplest one and is described briefly in the following section.

In Hall-Williamson method, it is assumed that the line broadening \( \beta \) of a Bragg reflection \((hkl)\) originating from the small crystallite size follows Scherrer equation.

\[
D = \frac{K\lambda}{\beta \cos \theta}.
\]

Here \( K \) is the shape factor, \( \lambda \) is the X-ray wavelength, \( \theta \) is the Bragg angle and \( D \) is the grain size. Also, the strain induced broadening \( \beta_e \) is given by the Wilson formula as,\textsuperscript{70,73}

\[
\beta_e = 4\varepsilon \tan \theta
\]

Here \( \varepsilon \) is the micro-strain. In Hall-Williamson method it is assumed that the particle size and strain contributions to the line broadening are independent of each other and the observed breadth is simply the sum of the two. Hence by including the above two factors, the full width at half maximum \( \beta \) becomes,

\[
\beta = \frac{K\lambda}{D \cos \theta} + 4\varepsilon \tan \theta
\]
Fig. 3. XRD patterns of nanoparticles of CdS (a) sample annealed at 200°C (C_2), and (b) annealed at 250°C (C_3).
The above equation is the Hall-Williamson equation. Plotting the value of \( \beta \cos \theta / \lambda \) as a function of \( 4 \sin \theta / \lambda \) the micro-strain \( \varepsilon \) may be estimated from the slope of the line and the crystallite size from the intersection of the line with the vertical axis. Using the Hall-Williamson method the average grain sizes were found to be 3.3 and 4 nm for the samples C₁ and S₁, respectively. Figures 2 (a) and (b) shows the Hall–Williamson plot for the samples C₁ and S₁. The table 2 shows a comparison of the grain sizes obtained by Debye-Scherrer formula and Hall–Williamson method.

Table 2. Comparison of grain sizes obtained from Scherrer formula and H & W method

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Grain size obtained from Scherrer' formula (nm)</th>
<th>Grain size from H &amp; W method (nm)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>1.8</td>
<td>3.3</td>
<td>+0.03853±0.0009</td>
</tr>
<tr>
<td>S₁</td>
<td>2.9</td>
<td>4</td>
<td>+0.1035±0.00425</td>
</tr>
</tbody>
</table>

Figures 3 - 5 show XRD patterns of the samples annealed at different temperatures from 200 to 500°C. As the annealing temperature is increased the diffraction peaks became more intense and sharper. This is an indication of grain growth and increased crystallinity with temperature. Using Debye-Scherrer formula, the grain sizes of the samples are found to be 1.8 and 2.9 nm. Using Hall and Williamson correction the grain sizes of the respective samples become 3.3 and 4 nm. The grain size of the sample C₁ increased to 25 nm when the sample is annealed to 500°C. From the XRD patterns of annealed samples (Figures 3 - 5), it is clear that the cubic to hexagonal transformation starts at a temperature of 250°C. Phase transition in nanocrystalline systems have been reported to occur substantially lower temperature than that of bulk materials. This is because the large fraction of atoms on the
Fig. 4. XRD patterns of nanoparticles of CdS (a) sample annealed at 300° C (C₄), and (b) sample annealed at 350° C (C₅).
surface of the nanoparticles increases the total energy there by making it less stable as compared to bulk counterparts. In the present case, the cubic to hexagonal transformation of nanoparticles of CdS stars at about 250°C. Thus, a decrease of cubic to hexagonal transition temperature for CdS nanoparticles is understandable. A large number of reports are available in the literature on the phase transition of cubic CdS to hexagonal CdS. Most of the studies were on bulk CdS films. Similar studies were reported by Arora et al. on annealed samples of nanoparticles of CdS of grain size 5 nm in vacuum.

A possible explanation for the cubic to hexagonal transformation is as follows. The cubic structure of as prepared CdS nanoparticles is a non-equilibrium, meta-stable phase. This is reasonable as the method by which the samples were prepared is by rapid nucleation and growth from supersaturated solution. The rapidity of similar precipitation reactions has been proposed to explain the creation of amorphous particulates of otherwise crystalline materials. The cubic structure may result from its close similarity to a roughly spherical nucleus, expected at the initial state of nucleation, rather than the hexagonal structure. Stacking fault energies of 13 meV/atom for CdS free energy difference between the cubic and hexagonal structure is small, again supporting metastability. If metastability is the proper explanation, then annealing temperature allows activation of the structure to the lower energy, stable, hexagonal phase.

In order explain the above cubic (zinc blend) to hexagonal (wurtzite) transformation of CdS on annealing, consider the model of zinc blend and wurtzite lattices of crystalline phases of a semiconductor similar to CdS as shown in figure 8. In the process of phase transformation from the cubic to the hexagonal crystalline phase, white atoms must jump to positions marked u in the figure 8 (a). On rotation of 60° of the second (111) plane around the (111) direction, the white atoms move to hexagonal sites. In the movement from a cubic to a hexagonal position, the white atom should go from a minimum of the periodic potential to the next minimum. In the case of CdS, the cubic phase is the metastable phase and the hexagonal phase is the stable phase; therefore, if the Cd atoms are the white atoms in figure 8, they must go from a minimum to the next lower minimum by crossing a potential barrier. Thus the movement is a thermally activated process, and on increasing the temperature, more Cd atoms will cross the potential barrier. Supposing that only one atom jumps to a
Fig. 5. XRD patterns of nanoparticles of CdS (a) sample annealed at 400°C (C₆), and (b) Sample annealed at 500°C (C₇).
Fig. 6. XRD patterns of nanoparticles of CdS (a) sample annealed at $200^\circ$C ($S_2$), and (b) sample annealed at $300^\circ$C ($S_4$).
position like u in β-CdS (cubic), then this atom will be located in an interstitial position with respect to the α-CdS (hexagonal) crystalline lattice. In this manner a Cd interstitial – Cd vacancy ($I_{Cd} - V_{Cd}$) complex defect is created.

The additional peaks observed on annealing became very sharp and intense at 2θ values of 25.06, 28.4, 33, 38.4, 48 and 55.5° at about 300°C ($C_4$). The peaks at 2θ values of 26.9, 43.9 and 52.1° could be associated with either the (002), (103) and (112) reflections of the hexagonal phase or the (111), (220) and (311) reflections of cubic phase of CdS (figure 4a). The peaks at 2θ values of 25.06, 28.4 and 48° are exclusively associated respectively with the (100), (101) and (103) reflections of hexagonal CdS phase. The observation of peaks at 2θ values of 33, 38.4 and 55.5° indicates the formation of CdO phase at temperatures above 300°C. Such partial conversion of CdS to CdO phase have been reported by Narayanan et al. in the case of CdS thin films annealed in air at about 400°C for 2 hrs. In the present case, the temperature of partial conversion from CdS to CdO is less compared to bulk counterparts. This is because of the enhanced energy possessed by nanoparticles due to large surface to volume ratio, as explained earlier.

Thermodynamically, for the formation of CdO
\[ CdS + 1.5O_2 \rightarrow CdO + SO_2, \]
\[ F = -90 \text{ Kcal (at 25°C)}, \]
the possible reaction. Bootsma has suggested that between 250 and 500°C, the oxidation of CdS may be written as,
\[ CdS_z + 1.5O_2 \rightarrow CdO_zSO_2 \leftrightarrow CdO_z + SO_2. \]

It is evident from the figures 4b and 5a that at thermal annealing temperature of 350 and 400°C, the cubic CdS, hexagonal CdS and cubic CdO co-exist in the sample. From the figures 3 – 5, it is observe that, as the annealing temperature increases, the intensity of the peak at 28.4° corresponding to hexagonal phase of CdS increases. This implies that the percentage of hexagonal phase increases with annealing temperature. The appearance of peak at 2θ = 36.9° of hexagonal phase, when the sample was annealed at 500°C, stands a clear evidence for the above statement, as this peak is not detectable at lower temperatures. From the figure 5 (b), it is also observed that the peaks corresponding to CdO phase disappeared at an annealing temperature of 500°C and a new peak at 2θ value of 29.6°. This

48
Fig. 7. XRD patterns of nanoparticles of CdS (a) sample annealed at 400°C ($S_3$), and (b) sample annealed at 500°C ($S_6$).
is attributed to the formation of cadmium oxide sulphide sulphate (Cd$_5$S$_3$O$_6$) phase at 500°C by comparing with JCPDS values. Fukatsu et al. reported a new phase 2CdS.2CdO. CdSO$_4$ in the system Cd-S-O in addition to CdS, CdSO$_4$, CdO and 2CdO. CdSO$_4$. They synthesized by mixing CdS and 2CdO. CdSO$_4$ and subsequent heating in the temperature range 900-1100°C. By measuring the standard Gibb’s energy changes using emf measurements, they found that the new phase is formed in the temperature range 963-1015°C. The interplanar distances and the miller indices for various planes of “as prepared” and air annealed samples of CdS nanoparticles of the present study are given in table 3. The values for hexagonal CdS, cubic CdS and CdO are also given from JCPDS data (table 4).

Figures 6 and 7 show the XRD pattern of the sample S$_1$ annealed at different temperatures from 200 - 500°C. From the figures, we can observe that the peaks corresponding to CdO phase is not observed for the samples annealed at 300 and 400°C. But at an annealing temperature of 500°C, a large number of peaks are observed. The peaks other than those of CdS are identified as ones corresponding to the possible phases such as Cd(S$_2$O$_7$) and Cd$_5$S$_3$O$_6$.\[89\]  

Figure 8. Cubic and hexagonal representation of a lattice similar to that of CdS.
Table 3. Interplanar distances and miller indices for various planes of nanostructured CdS patricles of as-prepared sample C1 and C1 annealed at different temperatures.

<table>
<thead>
<tr>
<th>As prepared</th>
<th>Annealed at 200°C</th>
<th>Annealed at 250°C</th>
<th>Annealed at 300°C</th>
<th>Annealed at 350°C</th>
<th>Annealed at 400°C</th>
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<tbody>
<tr>
<td>d(A)</td>
<td>hkl</td>
<td>I</td>
<td>d(A)</td>
<td>hkl</td>
<td>I</td>
<td>d(A)</td>
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Table 4. Interplanar distances and the miller indices for various planes of bulk CdS crystals taken from JCDPS data.

<table>
<thead>
<tr>
<th>Hexagonal CdS</th>
<th>Cubic CdS</th>
<th>CdO</th>
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Figure 9. XRD patterns of as-deposited and N$^+$ ion implanted nanostructured CdS films
2.4.2 X-RAY DIFFRACTION (XRD) STUDY OF NANOSTRUCTURED CdS THIN FILMS

The X-ray diffraction (XRD) patterns of as-prepared and N⁺ ion implanted nanostructured CdS thin films are shown in figure 9. The XRD patterns show less intensity peaks which are broad indicating small grain size of the nanostructured CdS thin films. The peaks at 20 values of 25, 27 and 28.5° corresponding to the planes (100), (002), and (101) of the hexagonal phase of CdS. However, the relative intensity of these peaks do not agree with those of the standard CdS- hexagonal powder pattern. Such difference in the intensity ratio of thin films are known to arise from preferential orientation of the films. Enhanced intensity of (002) peak has been reported in the literature for the case of CdS thin films of hexagonal phase obtained by chemical deposition, spray pyrolysis and vacuum evaporation. The preferred growth direction of the films in these cases was along the c axis perpendicular to the surface; i.e, the (002) planes of the films were parallel to the substrate surface. However, in the present case, the possibility of overlapping of the reflection from (111) planes of cubic phase of CdS with that from the (002) planes of hexagonal phase causing an enhanced intensity of this peak cannot be ruled out since the 20 values of these peaks are ~ 26.5°. The crystal structure of chemically deposited CdS thin films has been reported in the literature as cubic, hexagonal, or cubic-hexagonal mixed phase. The XRD pattern of the N⁺ ion implanted CdS thin films in the present study did not show significant difference from that of the as-prepared films (figure 9). But the spectra of N⁺ ion implanted samples show a decrease in intensity of the peaks. This may be due to the lack of long range order on account of disordered regions produced on implantation.

2.4.3 THERMOGRAVIMETRIC ANALYSIS (TGA) OF CdS NANOPARTICLES

Thermogravimetric analysis were performed at a heating rate of 10°C/min. in the temperature interval from room temperature to 600°C under oxygen flow of 100 ml/min. using the instrument SDT-2960. Figure 10 depicts thermogram of as prepared CdS nanoparticles (sample C₁). A maximum mass loss of 8% is observed in the temperature
Figure 10. Thermogravimetric analysis (TGA) of as-prepared nanoparticles of CdS

Figure 11. Derivative thermogram of TGA analysis of as-prepared CdS nanoparticles (sample C1)

range 250 and 350°C. From the derivative curve (figure 11), it is readily observed that mass loss does not occur in one step but that several processes are involved.\textsuperscript{91}\ The peak observed in the derivative curve at about 50°C may be due to the loss of adsorbed water content in the
Fig. 12(a) HRTEM images of CdS nanoparticles (C1) showing different orientations of lattice planes.

contd....
Fig. 12(a) HRTEM images of CdS nanoparticles (C1) showing different orientations of lattice planes.
Figure 12(b). HRTEM images of CdS nanoparticles (C1) showing a single agglomerated particle

Figure 13. SAED pattern of CdS nanoparticles (C1)

Figure 14. FFT of CdS nanoparticles (C1)
sample. The mass loss in the temperature range 250 - 350°C may be identified as the fractional conversion of CdS to CdO. Above 350°C the residual mass of the sample was found to increase slightly and to reach a maximum value around 505°C. The increase in mass is ascribed to the formation of the new phase CdS$_3$O$_6$ in the sample. The presence of these phases were clearly identified from the XRD pattern of the sample.

2.4.4 TRANSMISSION ELECTRON MICROSCOPY (TEM)

In order to determine the size, shape, and crystal structure of the particles, high resolution transmission electron microscopic images were taken. Transmission electron microscopy was done using JEOL 3010 high resolution transmission electron microscope (HRTEM) operating at 300 keV. Solutions of the powder samples dispersed in a solvent by sonication were drop-coated on carbon coated copper grids and the solvent was allowed to evaporate under ambient conditions. The excess solvent was removed by vacuum drying.

Figure 12 - 14 shows typical HRTEM micrographs of CdS nanoparticles prepared by the method 1 discussed in the section 2.2 (sample C1) together with a micro view of agglomeration of particles with corresponding Fast Fourier Transform (FFT) and Electron diffraction (ED) pattern. The HRTEM images indicate that the CdS nanoparticles are nearly spherical with slight prolate deviations. The HRTEM images indicate a size distribution of the CdS nanoparticles with particles size ranging from 2 - 3 nm. The lattice planes in the HRTEM images of the particles indicates the crystallinity of the sample.$^{2,11,91,92,94}$ The HRTEM image of a single particle (figure 12) exhibits an interplanar distance of 3.36 Å, belonging to the (111) lattice planes of cubic phase, which is consistent with X-ray diffraction data. The electron diffraction pattern (figure 13) consists of a few relatively broad diffuse rings. The broad and diffuse rings indicate a very small grain size and the presence of strain in the sample. Knowing the camera constant, the prominent rings in the ED pattern were indexed and it was found that the rings corresponded to the prominent reflections of cubic phase of CdS. Aggregation of the CdS nanoparticles is also observed in
Figure 15. HRTEM images of CdS nanoparticles (S1) showing size distribution and different lattice planes.

contd....
Figure 15. HRTEM images of CdS nanoparticles (S1) showing size distribution and different lattice planes.
some regions. A single aggregated particle of about 17 nm consisting of nine CdS nanoparticles is also observed in the figure 12 (b).

Figure 15 shows a typical HRTEM images of the CdS nanoparticles prepared by the method 2 discussed in the section 2.2 (sample S$_1$). The HRTEM images indicate that the CdS nanoparticles are nearly spherical in shape. One can see clear crystal lattice fringes, which demonstrate the crystallinity of the nanocrystals and this result is compatible with that of XRD. The size distribution for the sample is less compared to the sample C$_1$ prepared by method 1 and the grain size ranges from 3 - 4 nm. The grain size obtained from HRTEM is in good agreement with that obtained from XRD analysis. From the close observation of the HRTEM image of an individual CdS nanocrystal, it evident that it is single crystallite in structure. The image of single particle consists of nearly 13 lattice planes and it exhibit an interplanar distance of 3.36 Å, belonging to the (111) lattice planes of cubic phase, which again consistent with X-ray diffraction data.

2.5 MORPHOLOGICAL ANALYSIS OF NANOSTRUCTURED CdS THIN FILM

2.5.1 SCANNING ELECTRON MICROSCOPY (SEM)

High resolution scanning electron microscopy (HRSEM) provides a close look at the morphology of film surface. It usually produces images down to length scales of approximately 10 nm and provides valuable information regarding the structural arrangement, spatial distribution and geometric features of nanostructured materials. The details of as-deposited and N$^+$ ion implanted CdS films were studied using Hitachi S 2400, Scanning Electron Microscope (SEM). It is seen from the photographs (figures 16 and 17) that the surface of the as deposited film is smooth and consists of uniformly dispersed clusters. It has been shown in figure that all the particles are not exactly single crystal grains, but there are a large number of agglomerated grains. The agglomerated particles are of elongated grains with flat and plate-like grains structures.
Figure 16: High resolution scanning electron microscopic photographs of as-prepared nanostructured CdS thin film (CT1) prepared by CBD technique.

S4800 10.0kV 8.2mm x 80.0k SE(U, LA0) 500nm

S4800 15.0kV 8.2mm x 70.0k SE(U, LA0) 500nm

contd....
Figure 16. High resolution scanning electron microscopic photographs of as-prepared nanostructured CdS thin film (CT1) prepared by CBD technique.
Fig. 16. High resolution scanning electron microscopic photographs of as-prepared nanostructured CdS thin film (CT1) prepared by CBD technique.

Fig. 17. Scanning electron microscopic images of nitrogen ion implanted nanostructured CdS thin film.
2.5.2 RUTHERFORD BACKSCATTERING SPECTROMETRY (RBS)

Surface of thin films are usually characterized by electron microscopy (low depth resolution), ion spectroscopy (high depth resolution) and optical spectroscopy. Other important techniques for the characterization of surfaces are atomic force microscopy (AFM), Rutherford backscattering spectrometry (RBS) and ellipsometry. Among these techniques, RBS has the specific advantage that in addition to being non-destructive and capable of measuring thickness and giving information on film surface roughness, it can estimate the composition of the film.\(^{96-98}\)

In general, RBS work is carried out at lower energies (2-3 MeV) using \(^4\)He ions as the scattering cross-sections for most of the elements are Rutherford (Coulomb's law applies). However, the use of a higher energy \(^4\)He beam also has certain advantages: (i) the overlap between the backscattered peaks is reduced and (ii) it is particularly suited for multi-component films for which the stopping power decreases with increasing incident energy, resulting in narrower peaks in the backscattered spectrum; hence it is possible to accurately estimate the relative composition. The disadvantage is that the scattering cross-section is more likely to become non-Rutherford and, in fact, the value deviates by 4%. In the present study, the Rutherford backscattering measurements were carried out using 2 MeV alpha particles from 1.7 MV Tandetron accelerator. The backscattered particles were detected at 165° to the beam direction.

Figure 18 (a) and (b) shows the RBS spectra of two as-deposited nanostructured CdS thin films prepared by CBD under the same conditions. The RBS spectra of two samples prepared under the same conditions are presented (figure 18) to show the reproducibility of the method of preparation. The Cd edge is located in the spectra consistently at the 809 channel, whereas the S-edge is located at the 559 channel, implying uniform surface coverage for the films prepared by CBD technique. The Si-edge as seen in the spectra is contributed by the glass substrate as a result of the small thickness of the films. The Cd-peak is very sharp and shows no tapering towards the lower energy side. This is an indication of small value of the thickness and smoothness of the surface of nanostructured CdS thin films. The smoothness of the surface of the film is also seen from the SEM photograph shown in figure 15.
Figure 18 (a). RBS spectrum of as-prepared nanostructured CdS thin film

Figure 18 (b). RBS spectrum of as-prepared nanostructured CdS thin film
The relative concentration of Cd and S in the films can be estimated using the relationship,

\[
\frac{x}{1-x} = \frac{H_{CdS}}{H_S} \frac{d\sigma_{S}}{d\sigma_{Cd}} \frac{\varepsilon_{CdS}}{\varepsilon_S}
\]  

(1)

where \(x\) and \(1-x\) are the fractional atomic concentrations of Cd and S, respectively. The other quantities \(H\), \(\sigma\) and \(\varepsilon\) are the edge - heights, scattering cross-section (\(Z^2\) dependent) and resultant stopping power of Cd and S in CdS thin film. In the present context, the edge heights are replaced by the respective integrated counts under the Cd or S peak area. The average film thickness can be estimated from the relationship,\(^97\)

\[
\Delta t = \frac{\Delta E}{\varepsilon_{CdS}}
\]

(2)

where \(\Delta t\) and \(\Delta E\) are, respectively, the loss of the energy of the incident beam in traversing from the surface to the depth of the film and \(\varepsilon_{CdS}\) is the resultant stopping power of Cd or S in CdS and was calculated from XRUMP program. The relative compositions of Cd and S, and thickness of the film were calculated using relationship 1 and 2. The thickness of the two CdS films for which the deposition time of 25 minutes were found to be 102 nm and 104 nm. The relative composition of Cd:S in the films was found to be of 52:48. These results showed that the method of preparation of CdS thin films was highly reproducible.

2.6 CONCLUSIONS

In this chapter a detailed account of preparation of nanoparticles of CdS of two different grain sizes by controlled chemical route and their structural and morphological characterization are presented. The preparation and characterization of as-deposited and N\(^+\) ion implanted nanostructured CdS thin films by CBD technique is also discussed. We have prepared CdS nanoparticles of two different grain sizes. Using XRD analysis the grain sizes of the samples are found to be 1.8 and 2.9 nm. Using Hall and Williamson correction the
sizes of the respective samples becomes 3.3 and 4nm. From the HRTEM images the grain sizes of the corresponding samples are found to be 2-3 and 3-4 nm. XRD patterns show that the as-prepared samples of nanoparticles of CdS are cubic phase. Thermal annealing causes a structural transition from cubic to the hexagonal structure. Using thermogravimetric analysis, a maximum mass loss of 8% is observed in the temperature range 250 to 350°C. The SEM pictures of the as prepared and N⁺ ion implanted nanostructured CdS thin film show that the film surface is smooth and consists of uniformly dispersed clusters. The thickness of as prepared nanostructured CdS thin film was found to be 102 nm using RBS data. The relative composition of Cd:S in the films was found to be of 52:48.

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