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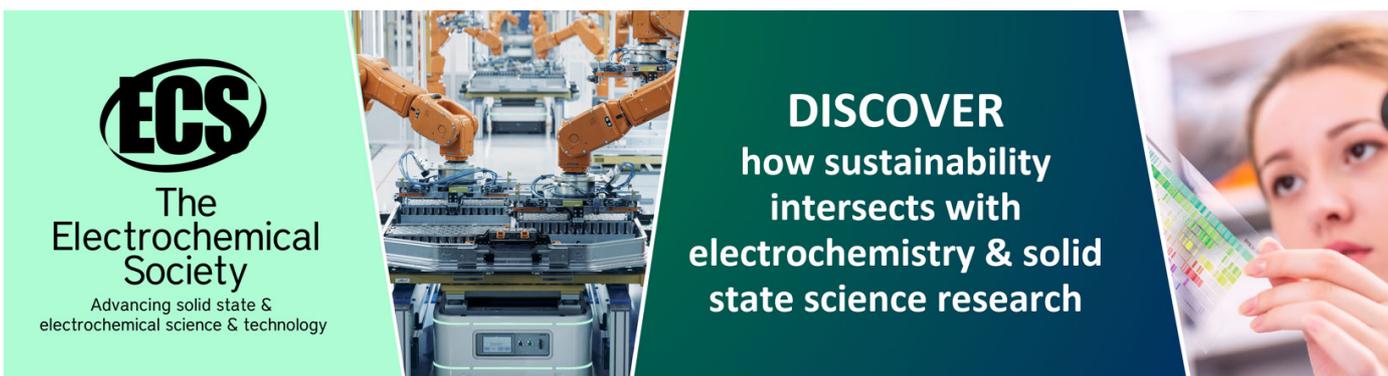
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Band gap shift, structural characterization and phase transformation of CdSe thin films from nanocrystalline cubic to nanorod hexagonal on air annealing

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Abstract

Cadmium selenide (CdSe) thin films were deposited on a glass substrate using the chemical bath deposition method at room temperature. The films were deposited using cadmium acetate as a Cd²⁺ ion source and sodium selenosulfate as a Se²⁻ ion source. The 'as-deposited' CdSe thin films are red in colour and specularly reflective. The 'as-deposited' CdSe layers grew with nanocrystalline cubic phase along with some amorphous phase present, with an optical band gap 'E_g' of 2.3 eV and electrical resistivity of the order of 10⁵–10⁶ Ω cm. The 'as-deposited' film is annealed in air at 673 K for 4 h and the effect of annealing on structural, morphological, optical and electrical properties is studied. It is worth noting that after annealing, metastable nanocrystallite cubic phase transforms into stable well crystalline hexagonal phase and films show a 'redshift' of '0.6 eV' in their optical band gap 'E_g'. After annealing, the crystallites' size increases from 45 Å to 180 Å, which results in a decrease in electrical resistivity. These changes have been attributed to the crystallite size dependent properties of CdSe semiconductor thin films.

1. Introduction

The synthesis of binary metal chalcogenides of group A^{II}–B^{VI} semiconductors in a nanocrystalline form has been a rapidly growing area of research due to their important nonlinear optical properties, luminescent properties, quantum-size effect and other important physical and chemical properties [1]. The semiconductor nanocrystallites belong to the state of matter in the transition region between molecules and solids. Their physicochemical properties are found to be strongly size dependent. Presently, nanocrystalline materials have opened a

new era in the field of electronic applications and information storage and processing, since the nanocrystalline material properties could be altered by changing the crystallite size and/or thickness of the film [2]. The properties of materials prepared by different methods are critically dependent on the preparation techniques and subsequent heat treatments, like annealing in air, vacuum or different gaseous environments such as H₂, N₂, Ar etc. Cadmium selenide is a widely used A^{II}B^{IV} group semiconductor whose band gap (E_g = 1.7 eV) lies in the solar energy spectrum [3]. Cadmium selenide has been studied intensively in recent years because of its potential use as a photoanode in photoelectrochemical (PEC) cells [3, 4–7]. The conversion efficiency of these cells as well as the physicochemical stability of the anode electrolyte system

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depends critically on the structure and the composition of the CdSe film. An essential criterion for obtaining high efficiency from PEC cells is use of the CdSe photoanode as a thin film with large size crystallites preferably in a hexagonal crystalline phase. The larger crystallites inhibit photo-carrier losses due to grain boundary recombination, and the hexagonal phase has a higher photo-absorbance and provides much needed stability against corrosive electrolyte in PEC cells [8]. A variety of techniques such as electrodeposition, thermal evaporation and chemical bath deposition [3, 9–12] have been used for deposition of CdSe thin films. Among various other methods, the chemical bath deposition (CBD) method is found to be a cheap and simple way to deposit large area nanocrystalline as well as polycrystalline metal chalcogenide thin films. The properties of materials prepared by the CBD method are critically dependent on various preparative parameters such as the sources and concentration of metal and chalcogenide ions, the pH of the resultant solution, deposition time, temperature etc and subsequent heat treatments, like annealing in air, vacuum or different gaseous environments such as H₂, N₂, Ar etc.

The present studies are focused on the deposition of nanocrystalline cubic CdSe film using the CBD method and its modification into a hexagonal phase after air annealing. In order to get good quality CdSe films, the preparative parameters such as the concentration of cadmium, deposition time and pH were optimized. To study the effect of air annealing on the various film properties, films were annealed in air at 673 K for 4 h.

2. Experimental procedures

2.1. CdSe thin film formation

Cadmium selenide thin films were deposited onto glass substrates using the CBD method. The reagents used were analytical grade cadmium acetate, selenium, liquor ammonia and sodium sulphide supplied by SD Fine-Chem Ltd.

To obtain the deposition of thin films, 30 ml of 0.5 M cadmium acetate was taken in a 100 ml capacity glass beaker and 25% ammonia solution was slowly added to it with constant stirring. Initially, the solution becomes milky and turbid due to the formation of a Cd(OH)₂ suspension. Further addition of excess ammonia dissolves the turbidity and makes the solution clear and transparent, and also reduces Cd²⁺ in concentration. 30 ml of freshly prepared 0.25 M Na₂SeSO₃ was added slowly to this, and with constant stirring, the pH of the final reaction mixture was $\sim 10 \pm 1$. The solution was stirred for a few seconds and then transferred into another beaker containing a cleaned glass substrate inclined vertically at 20° to the walls of beaker. The bath solution was kept at room temperature (300 K). The substrate coated with CdSe thin films was removed at suitable intervals (3–24 h), flushed under running tap water, then rinsed with deionized water, dried in air and preserved in a plastic container. Films prepared by this method were uniform, well adherent to the substrates and red in colour. The CdSe thin films deposited for up to 15 h give maximum thickness (0.22 μm) and decrease thereafter due to the formation of an outer porous layer of CdSe that peels off the outer portion of film. The ‘as-deposited’ and annealed CdSe

film of maximum thickness (0.22 μm) was characterized by using the following techniques.

2.2. Characterizations of thin films

The CdSe film thickness was measured with the commonly used weight difference method. Crystallographic study was carried out using a Phillips PW-1710 x-ray diffractometer using CuKα radiation in the 2θ range from 20° to 100°. The microstructure of the CdSe thin films on the glass substrate was studied by using a scanning electron microscope (Cambridge Stereoscan 250 MK-III) attached with an EDAX analyser to measure quantitatively the sample stoichiometry. The CdSe films were coated with a 100 Å gold palladium (Au–Pd) layer using a polaron SEM sputter coating unit E-2500, before taking SEM and EDAX. High-resolution transmission microscope (HR-TEM) analysis was performed with a Philips CM-12 electron microscope (point resolution 2.8 Å). For TEM and HR-TEM characterization, the thin film deposited on the glass substrate was scratched and placed on a gold grid of thickness 5 nm. A number of grids were prepared from the same sample in order to check reproducibility of the preparative procedure. An atomic force microscopy (AFM) unit (digital unit) was used to study the surface morphology and surface roughness of the film. In order to study optical properties, optical absorption spectra were recorded in the wavelength range of 300–850 nm using a UV-VIS-NIR spectrophotometer (Hitachi model-330, Japan). The dc electrical resistivity and thermoelectric power of the CdSe films were measured using a two-probe method in the temperature range of 300–500 K. The area of the films was defined (0.5 cm²) and silver paste was applied to ensure good ohmic contacts to the films.

3. Results and discussion

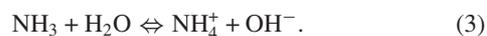
3.1. Reaction mechanism

The CdSe films are deposited from ammonia solutions using sodium selenosulfate as a Se²⁻ ion source and cadmium–ammonia complex ions as cadmium precursors. The deposition of CdSe thin films occurs; when ionic, a product of Cd²⁺ and Se²⁻ ions exceeds the solubility product of CdSe [$K_{sp} = 10^{-33}$]. The control of Cd²⁺ and Se²⁻ ions in the solution controls the rate of precipitation and hence the rate of film formation [13]. This is commonly achieved by using a stable complex for Cd²⁺ ions and a proper selenium ion source. The basic steps involved in the chemical deposition of a CdSe thin film are given below.

Sodium selenosulphate (Na₂SeSO₃) hydrolyses in solution to give Se²⁻ ions according to



Similarly, ammonia hydrolyses in water to give OH⁻ ions according to the equation,



When the ammonia solution is added to the Cd^{2+} salt solution, $\text{Cd}(\text{OH})_2$ starts precipitating when the solubility product (SP) of $\text{Cd}(\text{OH})_2$ is exceeded, i.e.



With $\text{SP} = [\text{Cd}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-14}$.

The $\text{Cd}(\text{OH})_2$ precipitate dissolves in excess ammonia solution to form the complex cadmium tetra-amine ions $[\text{Cd}(\text{NH}_3)_4]^{2+}$



Finally, the CdSe thin film formation takes place,



3.2. Growth mechanism

The growth mechanism of thin films using the CBD method can take place either in the bulk of the solution (homogeneous precipitation process) or at the substrate surface (heterogeneous process). Froment and Lincot [14] had proposed that the former is associated with the agglomeration of colloids formed in solution by the homogeneous reaction. It can be considered as a 'cluster by cluster' growth, leading to particulate films. The latter is a growth mechanism involving the reaction of atomic species at the surface; it corresponds to an atom by atom process, also called an 'ion by ion' process. They also reported that in practical situations both processes may interact, leading to films where colloids are included in the growing film. They also established a correlation between the growth mechanism and the phase or structure of the films from TEM and HR-TEM analyses. The predominance of one given mechanism is governed by the classical laws of homogeneous versus heterogeneous nucleation on a solid surface, involving the supersaturation ratio in the solution and the catalytic activity of the substrate [15]; in short, the growth mechanism depends on the experimental conditions.

In the present study CdSe films have been deposited at a relatively low temperature (300 K). Due to the low deposition temperature and slow rate of deposition, growth processes are based on the slow release of Cd^{2+} and Se^{2-} ions in the solution, which then condense with an 'ion by ion' basis on the substrates that are suitably mounted in the solution. This was confirmed later on with morphological characterization.

3.3. X-ray diffraction (XRD)

The CdSe thin films may grow with either sphalerite cubic (zinc-blende type) or the hexagonal (wurtzite-type) structure [16, 17]. The hexagonal state is the stable phase of CdSe while sphalerite cubic modification is a metastable structural phase commonly occurring at low temperature. Figures 1(a) and (b) give the XRD patterns of the 'as-deposited' annealed films. Figure 1(a) shows the XRD peak at $d = 3.505 \text{ \AA}$, $2\theta = 25.40^\circ$ and substantially broad at the base and another small intensity peak at $d = 2.147 \text{ \AA}$, $2\theta = 42.04^\circ$, that correspond to the (111) and (220) planes of metastable sphalerite cubic phase of CdSe [16]. The broad hump in the background is due to the amorphous glass substrate and also possibly due to some amorphous phase present in the CdSe thin film. Figure 1(b) shows that the annealed film exhibits a high intensity peak

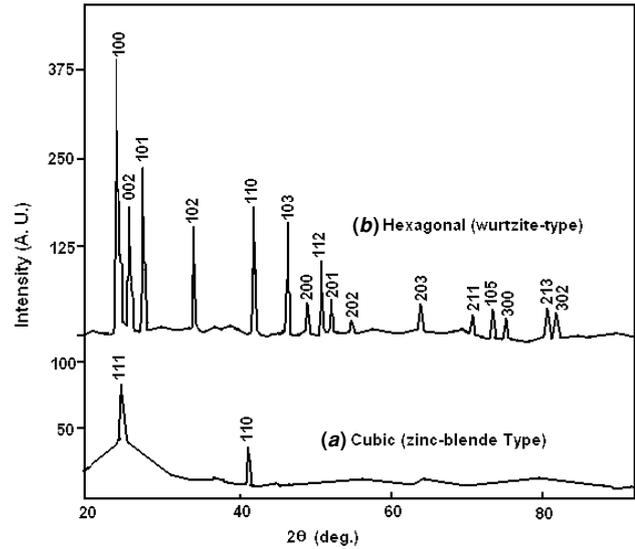


Figure 1. XRD patterns of CdSe films (a) 'as-deposited' and (b) annealed at 673 K.

Table 1. Comparisons of observed and standard 'd' values and their respective planes for 'as-deposited' and annealed thin films.

| Films | 'd' observed | 'd' standard | Planes |
|---------------------------------|--------------|--------------|--------|
| As-deposited' (cubic) | 3.505 | 3.51 | (111) |
| | 2.144 | 2.149 | (220) |
| 'Annealed at 673 K' (hexagonal) | 3.7305 | 3.72 | (100) |
| | 3.5165 | 3.51 | (002) |
| | 3.2948 | 3.29 | (101) |
| | 2.5545 | 2.554 | (102) |
| | 2.1514 | 2.151 | (110) |
| | 1.9818 | 1.98 | (103) |
| | 1.861 | 1.863 | (200) |
| | 1.8345 | 1.834 | (112) |
| | 1.7689 | 1.8 | (201) |
| | 1.6459 | 1.645 | (202) |
| | 1.4571 | 1.456 | (203) |
| | 1.3795 | 1.38 | (211) |
| | 1.3112 | 1.312 | (105) |
| 1.2416 | 1.2411 | (300) | |
| 1.2071 | 1.2055 | (213) | |

at $d = 3.7305 \text{ \AA}$, $2\theta = 23.75^\circ$. All other peaks and their relative planes are listed in table 1. The comparisons of observed 'd' values with standard 'd' values [17] clearly indicate the formation of the hexagonal (wurtzite-type) phase. The diffraction peaks in the XRD pattern of annealed samples are very sharp with the high intensity indicating the significant increase in crystallite size with the hexagonal modification. This behaviour indicates the phase transformation from the 'as-deposited' metastable nanocrystalline cubic phase of the CdSe film to the stable polycrystalline hexagonal after air annealing. Thus after annealing the film at a higher temperature, recrystallization takes place and the hexagonal polycrystalline phase prevails over the amorphous and/or nanocrystalline one. The occurrence of phase transformation is probably due to the increase in crystallite size and the change in atomic configuration of the CdSe thin films. Ndiaye *et al* [18] have reported the transition of chemically deposited amorphous CdSe thin films to hexagonal after CdCl_2 treatment at 723 K. It is also interesting to note that the phase transformation

of cubic to hexagonal CdSe in bulk takes place at high temperature (>1273 K) but that here the temperature of phase transformation is very low as compared to the bulk value; such a phase transition may occur at relatively low temperatures due to a change in the atomic configuration, since smaller crystallite size and larger surface area seem to favour the phase transformation [19]. Zelaya-Angel *et al* [20] also reported the phase transition of chemically deposited CdS thin films from cubic to hexagonal after thermal annealing in S_2 and $S_2 + Ar$ atmosphere, when the annealing temperature is >623 K.

The various structural parameters calculated for the films are given below.

3.3.1. Lattice parameters. The lattice constants ' a ' for cubic and ' a ' and ' c ' for hexagonal phase structure were determined from the relation

Cubic:

$$1/d_{hkl}^2 = (h^2 + k^2 + l^2)/a^2 \quad (7)$$

Hexagonal:

$$1/d_{hkl}^2 = 4/3\{(h^2 + hk + k^2)/a^2\} + (l^2/c^2). \quad (8)$$

The lattice constants are calculated by taking an average of all the observed diffraction XRD peaks. The average lattice constant ' a ' for the cubic phase was found to be 6.071 \AA , which is slightly less than the standard value (6.08 \AA) calculated from standard ' d ' values [17], indicating that the as-deposited films are under a compressive strain. The lattice constants ' a ' and ' c ' for the hexagonal phase were found to be $a = 4.308 \text{ \AA}$ and $c = 7.036 \text{ \AA}$ and the corresponding $c/a = 1.7415$, which is slightly higher than the standard value (1.6362) of the hexagonal structure [21]. This indicates that an annealed film is under tensile strain. Similar results have been reported by Pantoja and Mathew [22] for chemically deposited CdS thin films.

3.3.2. Crystallite size (D) and residual strain (ϵ'). During film deposition and post-deposition treatments, there is always a possibility of the development of strain (stress), which affects the mechanical properties of the films such as the stability of the microstructure, the adhesion between the film and the substrate and the opto-electronic properties of the deposited films. Strain (stress) in a film can be intrinsic, caused by the conditions prevailing during deposition (temperature, pH of solutions, deposition rate, concentration, impurities, etc). On the other hand, strain (stress) can be extrinsic to the film, but intrinsic to the composite film–substrate system, caused by the difference in thermal expansion coefficients [23]. The crystallite size and the residual strain are calculated from the FWHM using the relation [24] for cubic and hexagonal phases

$$\beta_{2\theta} \cos \theta = (K\lambda/D) + 4\epsilon' \sin \theta \quad (9)$$

where θ is Bragg's angle, $\beta_{2\theta}$ is the FWHM, $\lambda = 1.5406 \text{ \AA}$ for the $CuK\alpha$ radiation, D is the average diameter of CdSe crystallite, K is the shape factor and is approximately unity and ϵ' is the residual strain of the films. A plot of $\beta_{2\theta} \cos \theta$ versus $\sin \theta$ will give a straight line and the grain size D and ϵ can be calculated from the intercept and slope, respectively. The average crystallite size and residual strain were found to be 45 \AA , -1.428×10^{-4} and 180 \AA , 1.36×10^{-4} for cubic and hexagonal phase, respectively. The increase

in crystallite size shows the improvement in crystallinity that decreases the grain boundary discontinuities. The negative value of residual strain for as-deposited film indicates the compressive strain and the plus sign of an annealed film indicates tensile strain. If the thin film is deposited free from impurities, the compressive strain is generated at the thin film substrate interface, when the very small crystallites are bonded to substrates due to the surface tension effect. Also, we conclude that, due to the sufficient thickness of films, compressive strain may be generated in the grain boundary model when the adjacent surfaces of two grains come into contact during growth without coalescence, due to the low deposition temperature (300 K). The origin of compressive strength in 'as-deposited' thin film was not fully understood, but it may be due to the adhesive forces between the glass materials and deposited CdSe thin film that may result in compressive types of strength when films are deposited at lower temperature (300 K). Also, strain is generated in the grain boundary model when the adjacent surfaces of two grains come into contact during growth. The tensile strain developed in an annealing film may be due to the difference in thermal expansion coefficients of the substrate and deposited material and/or an annealing causes vacancies to diffuse to the surface of the film. In particular, the observed stress may be due to a loss of initial concentration by 1 or 2% that creates vacancies.

The quantitative analysis of the film was carried out by using the EDAX technique for 'as-deposited' CdSe thin films deposited on a glass substrate, at different points to study the stoichiometry of the film. Figure 2 shows a typical EDAX pattern and details of relative analysis for 'as-deposited' CdSe film. The elemental analysis was carried out only for Cd and Se; the average atomic percentage of Cd:Se was 50.5:49.5, showing that the sample was slightly Se^{2-} deficient. The Au peaks were due to gold sputtering over the film surface.

3.4. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a convenient technique to study the microstructure of thin films. The SEM of 'as-deposited' films is shown in figures 3(a), (b). From the micrograph (figure 3(a)), it is observed that the 'as-deposited' films are homogeneous, without cracks or holes and that they cover the glass substrate well. From the surface morphology of figure 3(b), we clearly observe the small spherical nanosized grains engaged in a fibrous-like structure, which clearly indicates the nanocrystalline nature along with some amorphous phase of CdSe thin films. The overgrowth of particles was also observed at few places. Grozdanov *et al* [25] also reported the mixture of nanocrystalline and amorphous phases for chemically deposited PbSe films and an increase in crystallinity after air annealing (24 h, 403 K). The SEM of an annealed film in air at 673 K (figures 4(a) and (b)) clearly shows the conversion of nanograins into well elongated, needle-shaped nanorods. The SEM study reveals that when the film is annealed at 673 K, all the nanorods are strongly oriented in the plane perpendicular to the substrate surface. They are united together at the base, but separate when coming out from the substrate. They form the cauliflower-like structure that looks like it has grown and/or originated from the surface of substrate. But from careful analysis, it is also observed that

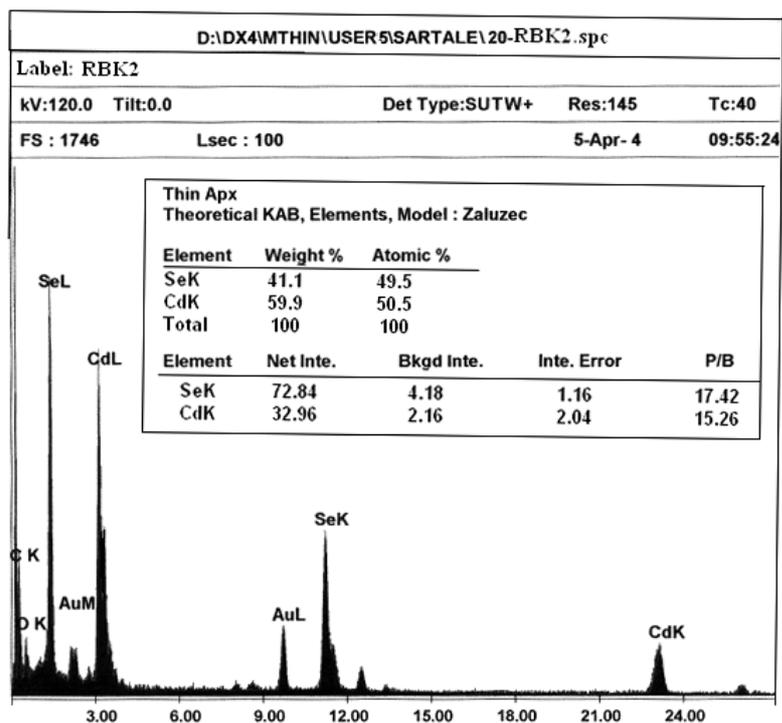


Figure 2. Typical EDAX pattern of 'as-deposited' CdSe film.

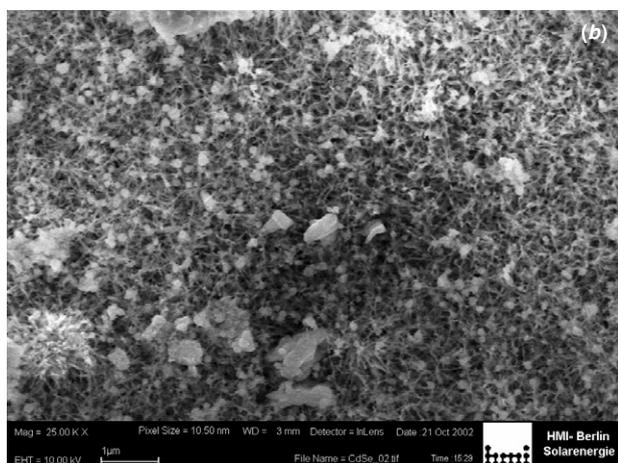
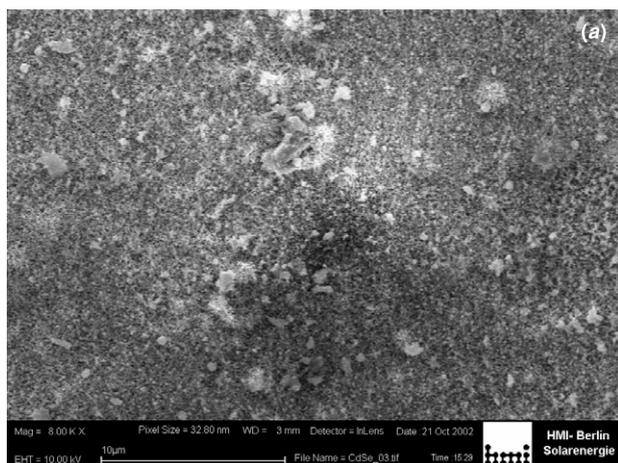


Figure 3. SEM of 'as-deposited' CdSe film: (a) 8 KX and (b) 25 KX.

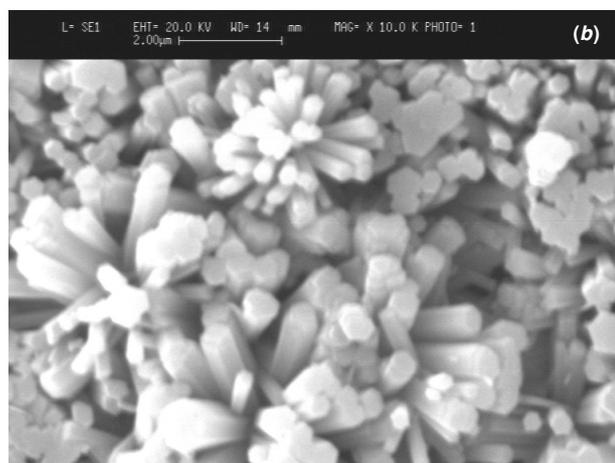
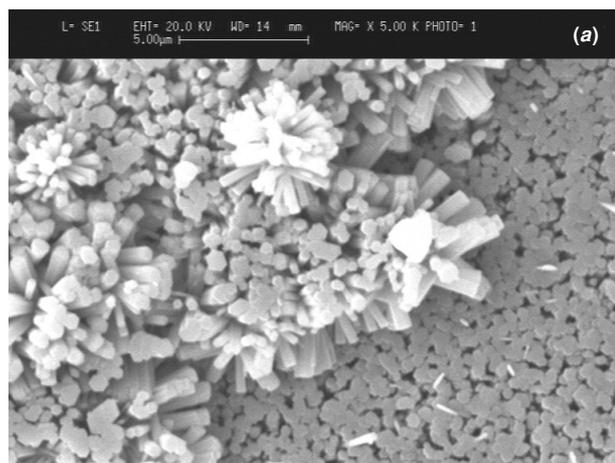


Figure 4. SEM of CdSe film annealed at 673 K: (a) 5 KX and (b) 10 KX.

in figure 4(b) there are also some dense regions of hexagonal phase of CdSe film whose c -axis is parallel to the substrate surface. Thus, we conclude that the c -axis of hexagonal phase is strongly oriented either parallel or perpendicular to the substrate surface. From SEM microstructure, we can draw the following main conclusions. (i) Due to air annealing, a number of grains and/or crystals diffused or united together to effectively form larger grains in the form of nanorods whose c -axis was perpendicular to the substrate surface along with some dense regions whose c -axis was parallel to the substrate surface. (ii) The CdSe grains have a large diffusion coefficient so that a number of grains diffused or coalesced together to form obviously larger grains. (iii) Larger surface area and a small thickness increase the surface to volume ratio that favours crystal phase transitions from a mixture of the amorphous and metastable nanocrystalline sphalerite cubic phases (zinc blende type structure) to the stable polycrystalline hexagonal phase (wurtzite type structure) at a relatively low temperature. This was confirmed from XRD analysis. At this point, it is necessary to introduce a possible mechanism, owing to the thermal annealing effect on the phase transformation of CdSe. During the phase change, the atoms must go through a potential barrier. Since the cubic phase is the metastable structure for CdSe, and the hexagonal phase is the stable one, due to thermal energy, the atoms move from a relative minimum in the periodic potential. Such a type of cubic to hexagonal phase transformation mechanism was proposed by Lozada-Morales *et al* [26] for CdS. The movement of atoms has also been theoretically studied by Sullivan [27].

Surface morphology was also observed with AFM; figures 5(a) and (b) show two-dimensional (2D) and three-dimensional (3D) images of 'as-deposited' film. Figure 5(a) shows that the small spherical nanograins of approximately 4–6 nm size were uniformly distributed over the smooth homogeneous background of amorphous phase. The surface roughness is very small (6.5 nm) and was unavoidable due to the three-dimensional growth of film. Figure 5(b) shows the uniform deposition of film over the surface of the substrate with small nanograins that are uniformly distributed along with some bigger sized nanograins.

3.5. High resolution transmission electron microscope (HR-TEM) studies

HR-TEM is the primary method used to determine crystal size and its distribution, although the specimen preparation is nontrivial and destructive. The HR-TEM (figure 6(a)) clearly shows randomly oriented nanocrystals with average crystallite size 4 nm, in close agreement with the average crystallite size (4 nm) obtained from XRD studies. Variation of size and shape of the nanocrystallites were distinct features of the CdSe thin film. Thus, this clearly indicates that the growth process on the substrate takes place 'atom by atom' commonly called the 'ion by ion' method. Some of the amorphous matrix is clearly seen around some of the CdSe crystals. This demonstrates that CdSe film contains both nanocrystalline and amorphous phases with the same stoichiometry. The amorphous phase has a 'glue-like' function, holding CdSe nanocrystals together. The electron diffraction pattern (figure 6(b)) and Fourier analysis (figure 6(c)) showed the

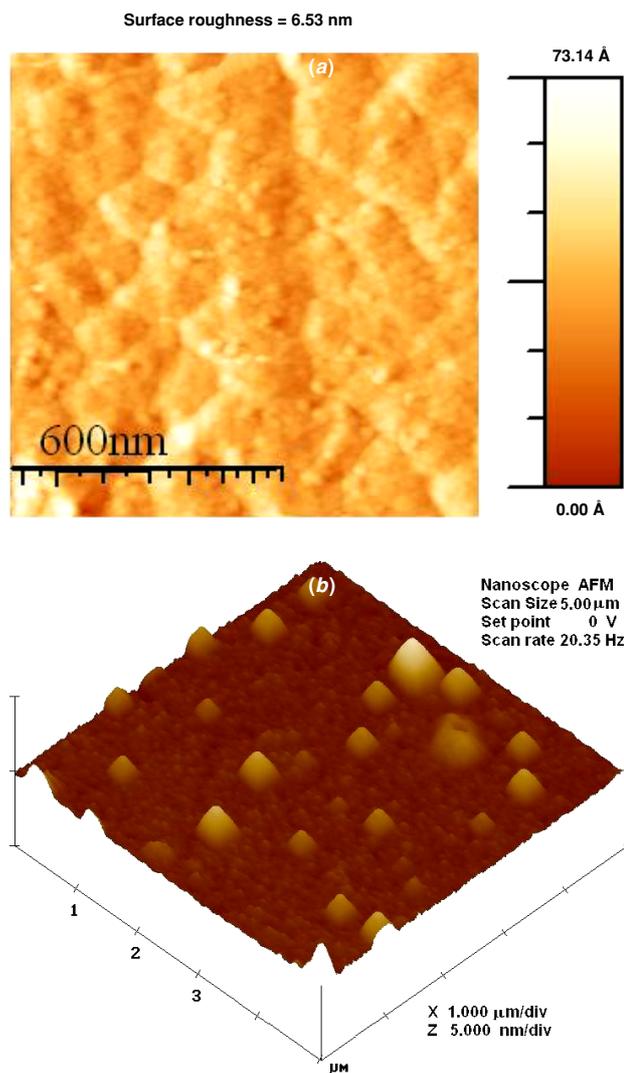


Figure 5. AFM images of 'as-deposited' CdSe film: (a) two-dimensional view and (b) three-dimensional view. (This figure is in colour only in the electronic version)

typical lattice spacing for cubic CdSe phase formation (for e.g. $hkl = 111$, $d = 3.51$ Å and 220 , $d = 2.15$ Å etc).

3.6. Optical absorption

The optical absorption spectra of CdSe films deposited onto a glass substrate were studied at room temperature in the range of wavelengths 350–850 nm. Figures 7 and 8 show the variation of optical absorbance (αt) and percentage transmission ($\%T$) with wavelength (λ), respectively. They show an increase in optical absorption and a decrease in transmission after annealing the film. This is possibly due to the increase in grain size, the decrease in the number of defects and the change in colour from red to black. It is clearly seen from the optical spectra that the absorption and transmission edge shifts towards a longer wavelength for annealed films. This shift indicates a decrease of the optical band gap 'Eg'. 'Eg' was calculated using the following relation:

$$\alpha = A(h\nu - E_g)^n / h\nu \quad (10)$$

where A is a constant and n is a constant, equal to $\frac{1}{2}$ for direct band gap semiconductors. The estimated band gaps

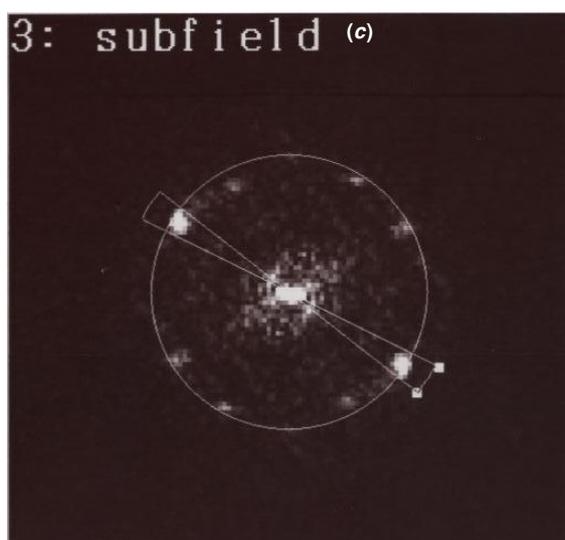
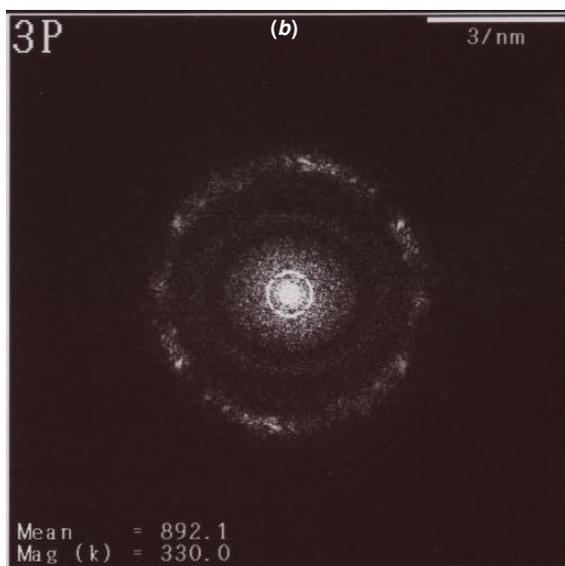
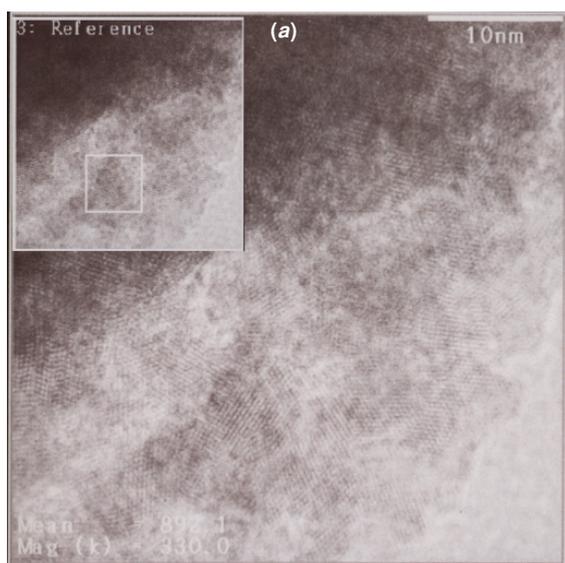


Figure 6. (a) HR-TEM (and reference used for it) of 'as-deposited' CdSe film, (b) electron diffraction pattern of figure 5(a) and (c) Fourier transformation of figure 5(a).

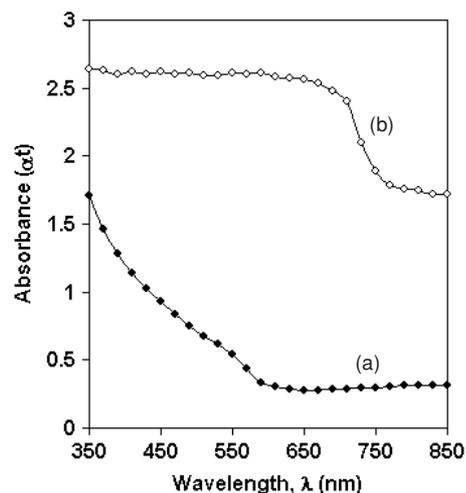


Figure 7. Plot of optical absorbance (αt) versus wavelength (λ) of CdSe films (a) 'as-deposited' and (b) annealed at 673 K.

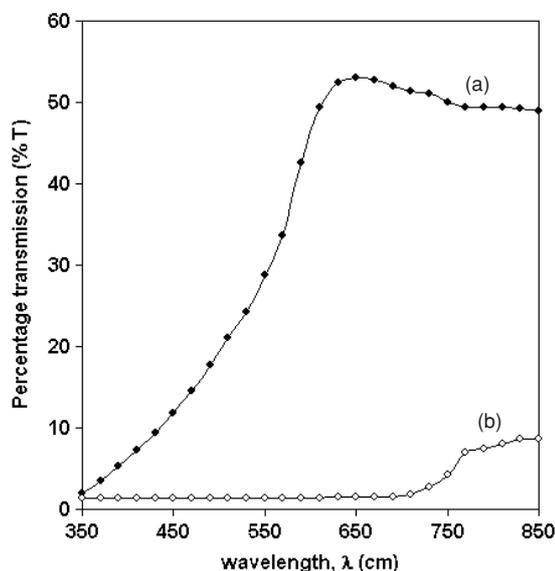


Figure 8. Plot of optical transmissions (% T) versus wavelength (λ) of CdSe films (a) 'as-deposited' and (b) annealed at 673 K.

from the plots of $(\alpha h\nu)^2$ versus $h\nu$ are shown in figure 9, for 'as-deposited' and annealed CdSe films. The linear nature of the plot indicates the existence of the direct transition. The band gap ' E_g ' was determined by extrapolating the straight portion to the energy axis at $\alpha = 0$. It was found to be 2.3 eV for as-deposited CdSe films and shows 0.6 'blueshift' from the normal bulk value (1.7 eV). This may be due to the nanocrystalline nature of CdSe thin film, where charges are localized in individual nanocrystals which results in an increase in band gap. The band gap of the annealed hexagonal CdSe thin film was found to be 1.7 eV, which is equal to the normal bulk value of hexagonal CdSe. The decrease in band gap from 2.3 eV to 1.7 eV shows that annealing the film causes a strong 'redshift' of 0.6 eV in the optical spectra to that of characteristic bulk CdSe, due to sintering of the nanocrystallites into larger crystallites and the change of phase from cubic to hexagonal that increases the

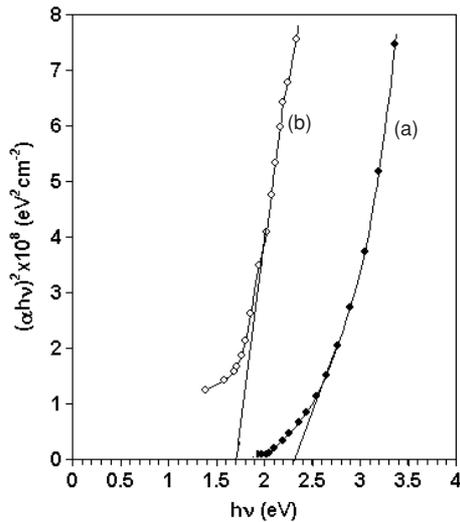


Figure 9. Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CdSe films (a) 'as-deposited' and (b) annealed at 673 K.

lattice parameter. Lozada-Morales *et al* [28] reported that while the lattice parameter increases, the optical band gap decreases. Hodes *et al* [11] reported that the band gap of wurtzite hexagonal phase is slightly less than in the sphalerite cubic phase of CdSe. These changes have been attributed to the crystallite size-dependent properties of the energy band gap. Similar 'blue/redshift' in band gap energy 'Eg' values for the films with smaller thickness and/or crystallite sizes have been reported for chemically deposited CdSe thin films [10–12].

3.7. Electrical resistivity

The dark electrical resistivity of 'as-deposited' and annealed CdSe films was measured at room temperature. It was found that the room temperature electrical resistivity of the film is $8 \times 10^5 \Omega \text{ cm}$ which then decreases to $6.23 \times 10^3 \Omega \text{ cm}$ after annealing the film at 673 K. It is well known that [29–31] electronic transport properties of thin polycrystalline semiconductor films are strongly influenced by their structural characteristics (the crystallite shape and size, inter-crystallite boundaries, lattice defects etc) and purity (nature and concentration of the impurities, adsorbed and absorbed gases etc). The variation of dc electrical resistivity of the 'as-deposited' and annealed CdSe was measured in the 300–500 K temperature range and shown in figure 10.

It can be observed (figure 10) that the $\ln \rho$ versus $10^3/T$ curves for as-deposited as well as annealed samples show

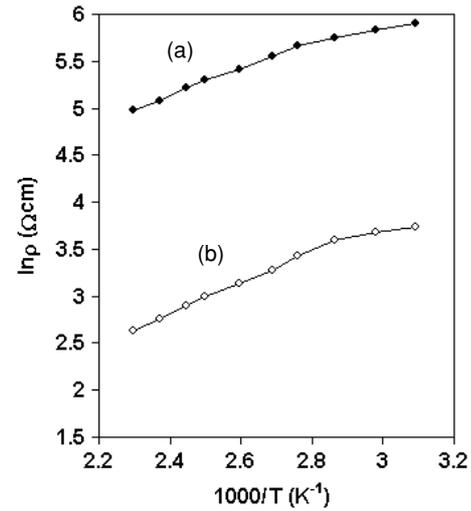


Figure 10. Plot of $\log \rho$ versus $1000/T$ of CdSe films (a) 'as-deposited' and (b) annealed at 673 K.

two linear portions. The first is at a lower temperature range ($T = 300\text{--}355 \text{ K}$) characterized by a smaller slope. In the higher temperature range the curves are characterized by a higher slope.

The temperature dependence of the electrical conduction can be described by the well-known exponential law,

$$\rho = \rho_0 \exp(E_a/kT) \quad (11)$$

where ρ_0 is a parameter depending on the sample characteristics (thickness, structure etc), E_a denotes the thermal activation energy of electrical conduction, k is Boltzmann's constant and T is absolute temperature.

In this case, the activation energy ' E_a ' varies from 0.86 to 0.34 eV for the lower temperature portion of the $\ln \rho = f(10^3/T)$ curve and 0.65–0.16 eV for the higher temperature portion.

The decrease in electrical resistivity and activation energies after annealing may be due to the change in structural parameters, improvement in crystallite and grain size, decrease in inter-crystallite boundaries (grain boundary domains) and removal of some impurities (adsorbed and absorbed gases). Excess atoms of compound are also possible [31], possibly due to a small change in stoichiometry after annealing. The thermoelectric measurement confirms well-known n-type semiconducting behaviour of CdSe thin films.

Table 2 depicts the various results obtained in the present investigation.

Table 2. Representation of crystallites size, lattice parameter, residual strain, band gap, electrical resistivity of 'as-deposited' and annealed thin films.

| Thin films | 'D' (Å) | Lattice parameters | | | 'Eg' (eV) | 'ρ' (Ω cm) |
|----------------|---------|--------------------|---------|------------------------|-----------|--------------------|
| | | 'c' (Å) | 'a' (Å) | 'ε' × 10 ⁻⁴ | | |
| 'As-deposited' | 45 | 6.071 | | -1.428 | 2.3 | 8×10^5 |
| Annealed | 180 | 7.032 | 4.308 | 1.36 | 1.7 | 6.23×10^3 |

D: crystallites size; ε': residual strain; Eg: band gap energy; ρ: resistivity at room temperature.

4. Conclusions

From the above studies, it is concluded that the CdSe thin films deposited by an aqueous alkaline medium at room temperature grow with nanocrystalline cubic phase, with band gap 2.3 eV and electrical resistivity of the order of $10^6 \Omega \text{ cm}$. Thermal annealing was found to increase the crystallinity of films along with a recrystallization process that changes the metastable nanocrystalline cubic (zinc-blende type) phase of CdSe into the stable polycrystalline hexagonal (wurtzite type) phase. Due to air annealing, the crystallite size of particle increases from 45 Å to 180 Å that results in a decrease in electrical resistivity and the film shows a 'redshift' of 0.6 eV in its optical spectra. Such dependence has been attributed to the crystallite size effect in chemically deposited thin films. Also, 'as-deposited' film is under compressive strain, while annealed film is under tensile strain. The n-type conductivity for as-deposited and annealed films were confirmed from thermoelectric measurement.

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