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Effects of annealing on cadmium selenide nanocrystalline thin films prepared by chemical bath deposition

T.S. Shyju, S. Anandhi, R. Indirajith, R. Gopalakrishnan*

Crystal Research Lab, Department of Physics, Anna University Chennai, Chennai 600025, India

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ABSTRACT

CdSe thin films were deposited on the glass substrates by chemical bath deposition method at 80 °C using cadmium acetate and sodium selenosulphate as source materials and ethylene diamine tetra acetic acid (EDTA) as a chelating agent with concentrations 0.025, 0.075 and 0.1 M. The various preparative parameters such as composition, solution temperature, pH of the solution and deposition time were optimized for depositing good quality CdSe films. The deposited CdSe thin films are annealed in the air atmosphere for 3 h at 350 °C. The structural, optical, morphological and electrical properties of as deposited and annealed samples were studied. The crystallite size of the film was estimated by Scherrer's formula and the dislocation density was evaluated using the high intense X-ray diffraction peaks. The phase change of CdSe from cubic to hexagonal after annealing at 350 °C was confirmed from the X-ray diffraction pattern. The thickness of the film is found to be 0.6 μm using interferometery technique. The optical properties were studied using UV–vis and photoluminescence spectrometer. The optical band gap of the film has been estimated to be 2.1 and 1.84 eV for as deposited and annealed films. The photoluminescence band shows red shift with increasing particle size after annealing at a higher temperature. The homogeneous crystalline grains were observed from SEM as well as AFM images. The as-deposited and annealed CdSe films exhibit negative Hall coefficient, which confirms n-type conductivity. The Hall mobility, resistivity, carrier concentration and conductivity were evaluated.

1. Introduction

Semiconductor nanocrystalline materials have been extensively investigated in the last decade because of their potential in many areas of research and technological applications. Semiconductor nanocrystallites belong to the state of matter in the transition region between molecules and solids. Their physical and chemical properties are found to be strongly size dependent [1–4]. Nanocrystalline semiconducting materials have been used in electronic, optoelectronic and solar energy conversion devices. CdSe is a direct band gap semiconductor belongs to II–VI group, possessing excellent optoelectronic properties. It is used as an n-type window layer material in thin film solar cells. Recently, Chate et al. [5] have reported that CdSe is the suitable candidate for photovoltaic applications [6,7].

The nanocrystalline forms of II–VI binary metal chalcogenide semiconductors are getting interest in research owing to their important luminescent properties, quantum size effect and other physical and chemical properties [8]. The deposition parameters such as pH, temperature, concentration of the solution and deposition time influence the formation of nanocrystalline thin films and crystallite size, which in turn engineer the band gap of the material [9]. EDTA is an amino derived organic compound known to be a strong chelating agent, which forms stable complexes with metal ions and dissociates reversibly at a low rate. Zhang et al. [10] and Padmavathy et al. [11] have used EDTA as chelating agent in the chemical bath and photochemical deposition of CdS thin films from the aqueous solution.

The deposition of CdSe thin films was made using different deposition methods such as, thermal evaporation [12], pulsed laser deposition (PLD) [13], electrodeposition [14], spray pyrolysis [4], successive ionic layer adsorption and reaction (SILAR) [15] and chemical bath deposition (CBD) [6,7,16,17]. Among these methods, CBD is one of the most promising methods for making large area high quality thin films for photovoltaic applications because it is an efficient and cost effective method. In the chemical bath deposition (CBD) method, deposition of metal chalcogenide semiconductor thin films occurs when the substrate is immersed in a chemical bath containing the metal ions with suitable complexing agent and chalcogenide ions.

In the present work CdSe thin films have been deposited on the glass substrates by chemical bath method at 80 °C using cadmium acetate and sodium selenosulphate as source materials and

* Corresponding author. Tel.: +91 44 2235 8710/8707; fax: +91 44 2235 8700.
E-mail addresses: krgkrishnan@annauniv.edu, krgkrishnan@yahoo.com (R. Gopalakrishnan).

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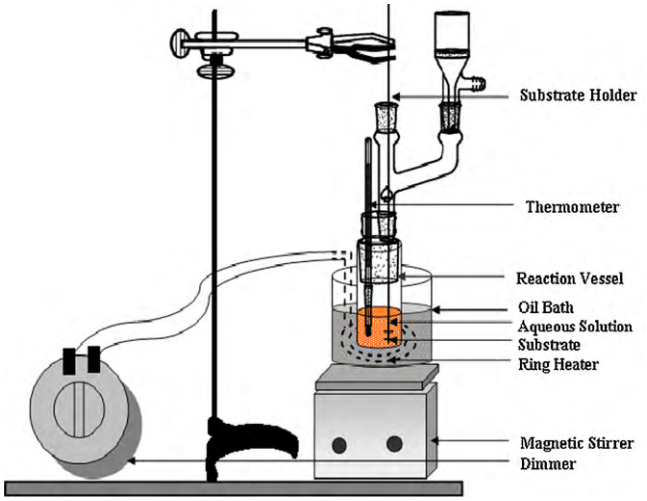

Fig. 1. Schematic diagram of presently used chemical bath deposition technique.

ethylene diamine tetra acetic acid (EDTA) as a chelating agent with different molar concentrations 0.025, 0.075 and 0.1. The addition of a small quantity of EDTA enhances the spreading of crystalline films during the deposition process without affecting the properties of material and increases the lateral growth of thin films. The deposited CdSe thin films are annealed in air atmosphere for 3 h at 350 °C and the structural properties of the films are studied. From the structural analysis it is inferred that 0.1 M EDTA added thin films are of good quality and the films are used for optical, electrical and morphological studies.

2. Experimental procedures

2.1. Substrate cleaning

The substrate cleaning is very important in the deposition of thin films. Commercially available glass slides with a size of 75 mm × 25 mm × 2 mm were washed using soap solution and subsequently kept in hot chromic acid and then cleaned with deionized water followed by rinsing in acetone. Finally, the substrates were ultrasonically cleaned with deionized water for 10 min and wiped with acetone and stored in a hot oven.

2.2. Processes involved in the chemical deposition

Chemical bath deposition technique for metal chalcogenide semiconductor thin films refer to the deposition of thin films on substrates kept in contact with dilute solution containing the metal and chalcogenide ions in chemical bath. The schematic diagram of chemical bath deposition is shown in Fig. 1. The chemical deposition of the CdSe thin film is due to the reaction between the slowly released selenide anion and cadmium cation. CdSe thin films were deposited on glass substrate by chemical bath deposition method using analytical grade $Cd(CH_3COO)_2$, 25% of liquid ammonia and freshly prepared Na_2SeSO_3 solutions. For the preparation of sodium selenosulphate (Na_2SeSO_3), the mixture of 0.5 mol/l of Na_2SO_3 and 0.2 mol/l of Se metal was stirred and refluxed at 90 °C for 24 h. The resultant product yielded clear solution of sodium selenosulphate [18].

The thin films were deposited using cadmium acetate (0.5 M) as Cd^{2+} ion source and sodium selenosulphate (0.125 M) as Se^{2-} ion source in the ratio of 1:1. 0.5 M cadmium acetate was dissolved in a reactant vessel and consequently ammonia solution was added drop-by-drop to adjust the pH in the range of 10–11 to set in the base medium with continuous stirring in order to dissolve the white precipitate of cadmium hydroxide. Ethylene diamine tetra acetic acid (EDTA) was used as a chelating agent with different molar concentrations like 0.025, 0.075 and 0.1 in the deposition process.

The EDTA was used to enhance the spreading of films during deposition, as it captures the metal ions from the solution, it gets saturated and releases the captured ions in the solution thereby increase the uniform lateral growth of thin films. The reactant vessel was kept in an oil bath, at a temperature of 80 °C with the help of a ring heater. Freshly prepared sodium selenosulphate was added into the solution slowly. A thermometer was placed in the solution to measure the temperature of the solution. Initially the solution appears to be colorless and becomes orange, subsequently the color of the solution changes from orange to dark red, which indicates the formation of CdSe nano particles. A glass substrate was placed vertically inside the vessel with the help of a suitably designed substrate holder. After a time period of 60 min, the glass slide was removed from the bath and cleaned with deionized water and dried in the hot oven. Uniform CdSe film with thickness of 0.6 μm was obtained, having good adherence, reddish in color and secularly reflective. Many trails were made by optimizing the deposition parameters to obtain a good quality CdSe thin film. Good quality CdSe thin films were subjected to characterization studies.

2.3. Reaction mechanism

The deposition process is based on slow release of Cd^{2+} and Se^{2-} ions in the solution, which then condense either ion by ion or cluster by cluster on the surface of the substrate. The deposition of CdSe occurs when the product of Cd^{2+} and Se^{2-} exceeds the solubility of CdSe. The decomposition of sodium selenosulphate is made possible in an aqueous alkaline medium containing ammonia as a complexing agent, which controls the release of Cd^{2+} ions in the reaction bath. Sodium selenosulphate hydrolysis [19] in the solution gives Se^{2-} ions according to the following reaction:

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^-$$

$$HSe^- + OH^- \rightarrow H_2O + Se^{2-}$$

when ammonia is added to the solution it forms a complex cadmium tetra-amine ion $[Cd(NH_3)^{2+}]$ as:

$$Cd^{2+} + 4NH_3 \rightarrow [Cd(NH_3)_4]^{2+}$$

Then the $[Cd(NH_3)_4]^{2+}$ reacts with Se^{2-} ions that results in the formation of CdSe thin films as follows:

$$[Cd(NH_3)_4]^{2+} + Se^{2-} \rightarrow CdSe + 4NH_3$$

In the initial stage of film formation, the source materials are sufficient and the solution has a high degree of supersaturation, the process of homogenous precipitation (ion-by-ion growth mechanism) in the solution plays an important role which leads to an increase in film thickness.

2.4. Annealing of CdSe thin films

The deposited film was subjected to annealing in the air atmosphere with the help of tubular furnace at 350 °C. The samples were kept in the tubular furnace and the temperature of the furnace was increased by 50 °C/h using Eurotherm temperature controller up to 350 °C. The samples were maintained at 350 °C for 3 h and the furnace was cooled to room temperature by 50 °C/h.

3. Results and discussion

3.1. Structural analysis

The structure of the deposited CdSe thin film was confirmed by XPERT-PRO X-ray diffractometer using CuKα$_1$ radiation (λ = 1.5418 Å) within the 2θ range 10–80°. The CdSe thin films may crystallize in wurtzite (hexagonal) structure or zincblende (cubic) structure [20,21]. Figs. 2 and 3 show the XRD patterns of as-deposited and annealed CdSe thin films deposited on the glass substrate by chemical bath deposition technique at 80 °C with EDTA as a chelating agent in various concentrations. From Fig. 2 it can be concluded that the crystallinity of the film increases with the addition of chelating agent in the depositing solution. The well defined peaks are observed in the XRD pattern. The XRD results reveal that the deposited CdSe thin films are polycrystalline in nature with cubic structure having (1 1 1) plane as the preferred orientation [20]. The low intensity peaks show that the as-deposited CdSe thin films are coarse crystallites. Fig. 3 shows the XRD patterns of the annealed samples at 350 °C using various concentrations of EDTA added CdSe thin films. The structure changes from cubic to hexagonal system with a high intense peak in (1 0 0) plane as preferred orientation [21]. Such a phase transition from cubic to hexagonal may occur due to change in atomic configuration, since smaller crystallite size and larger surface area appear to favor the phase transformation [22]. Estrada and co-workers [23] have reported similar observations for other metal chalcogenide thin films.

The crystallite size and dislocation density were calculated from high intense diffraction peak. Table 1 shows the observed interplanar spacing (d) and their possible identification in comparison with

Table 1
Structural parameters of as-deposited CdSe thin films.

EDTA concentration (M)	2θ	(hkl)	d-Spacing (Å)		Crystallite size (nm)	Dislocation density (δ) × 10^{16} lines/m^2
			JCPDS	Observed		
0.1	25.7	1 1 1	3.49	3.50	4.06	6.06
	42.6	2 2 0	2.13	2.11	–	–
	49.8	3 1 1	1.82	1.83	–	–
0.075	25.9	1 1 1	3.49	3.44	3.2	9.76
	42.6	2 2 0	2.13	2.11	–	–
	50.2	3 1 1	1.82	1.81	–	–
0.025	26.0	1 1 1	3.49	3.42	2.5	16.00
	42.7	2 2 0	2.13	2.11	–	–
	50.2	3 1 1	1.82	1.81	–	–

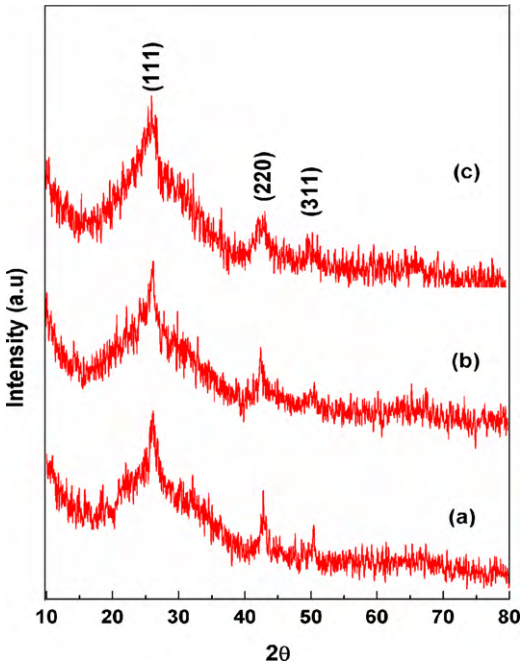

Fig. 2. XRD pattern of as-deposited CdSe thin films for various concentration of EDTA, (a) 0.025, (b) 0.075 and (c) 0.1.

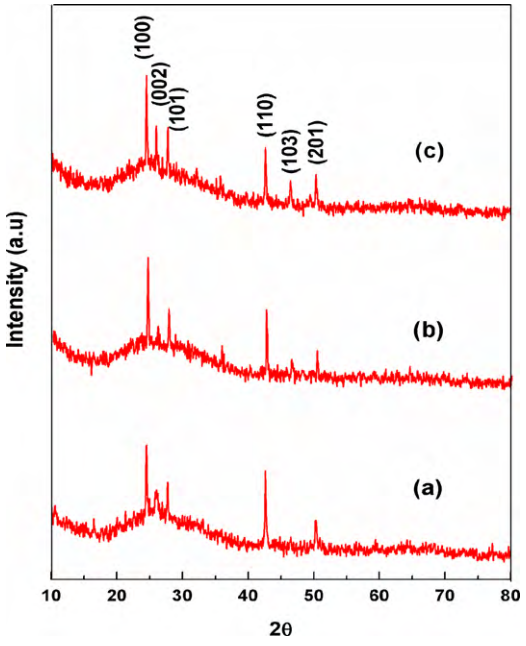

Fig. 3. XRD pattern of CdSe thin films annealed at 350 °C, (a) 0.025, (b) 0.075 and (c) 0.1.

standard d-values taken from Joint Committee on Powder Diffraction Standards (JCPDS) data file [20]. The size of the crystallites is evaluated from the high intense peak of the X-ray diffraction pattern by a Gaussian fit, using the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where β is the full width at half maximum, λ is the wavelength of X-ray used, θ is the Bragg's angle. The dislocation density (δ) has been determined using Williamson and Smallman's formula [24]. The dislocation density was calculated from the crystallite size of the deposited samples and the values are tabulated in Tables 1 and 2.

$$\delta = \frac{1}{D^2} \quad (2)$$

3.2. Optical properties

3.2.1. UV–vis analysis

The thickness of the film was determined by an optical interference technique and it is found to be of the order of 0.6 μm. The transmittance spectrum of the CdSe film was recorded using UV–vis double beam spectrophotometer at room temperature in the wavelength range 300–1000 nm. Optical transmittance of the film is shown in Fig. 4. From the optical transmittance spectra it is observed that the transmittance of the film reduces after annealing at 350 °C, owing to the color change and increase in the particle size of the film after annealing. Optical investigations of films reveal that there is a band to band direct transition. The absorption data

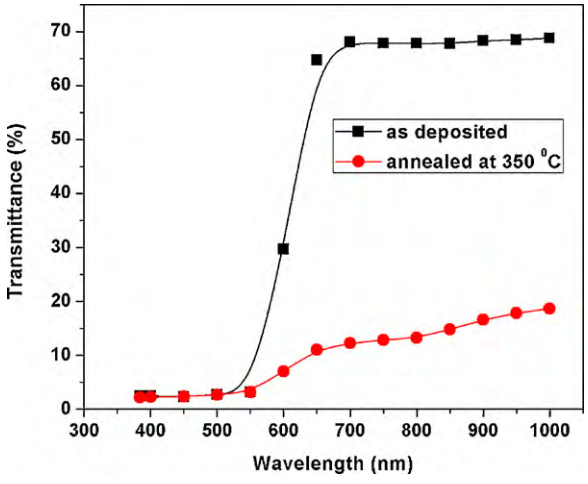

Fig. 4. Optical transmittance spectra of as-deposited and annealed CdSe thin films.

Table 2
Structural parameters of 350 °C annealed CdSe thin films.

Annealed at 350 °C	2θ	(hkl)	d-Spacing (Å)		Crystallite size (nm)	Dislocation density (δ) × 10^{14} lines/m^2
			JCPDS	Observed		
0.1	24.56	1 0 0	3.72	3.81	51.9	5.28
EDTA	26.03	0 0 2	3.50	3.42	61.0	2.68
	27.77	1 0 1	3.28	3.22	41.0	5.94
	42.66	1 1 0	2.14	2.12	33.0	9.18
	46.47	1 0 3	1.97	1.95	35.1	8.11
	50.38	2 0 1	1.79	1.81	29.3	11.64
0.075	24.50	1 0 0	3.72	3.63	45.4	4.85
EDTA	26.03	0 0 2	3.50	3.42	55.1	3.28
	27.77	1 0 1	3.28	3.22	36.2	7.63
	42.62	1 1 0	2.14	2.12	40.2	6.18
	46.48	1 0 3	1.97	1.95	26.6	14.13
	50.33	2 0 1	1.79	1.81	38.8	6.64
0.025	24.54	1 0 0	3.72	3.63	41.0	5.94
EDTA	26.06	0 0 2	3.50	3.42	37.2	7.22
	27.77	1 0 1	3.28	3.22	40.3	6.13
	42.66	1 1 0	2.14	2.12	32.2	9.63
	20.34	2 0 1	1.79	1.81	32.1	9.66

were analyzed using the classical relation for near edge optical absorption of semiconductors.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (3)$$

where $h\nu$ is photon energy, E_g is band gap and A is constant.

Now n in the Eq. (3) can have values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively.

The band gap energy (E_g) is determined by plotting a graph of $h\nu$ vs $(\alpha h\nu)^2$ (Fig. 5) for the direct band gap. The band gap 'E_g' was determined by extrapolating the straight line portion to the energy axis, whose intercept to the X-axis gives the optical band gap. The optical band gap is found to be 2.1 and 1.84 eV for the as deposited and the annealed CdSe films respectively. Due to annealing, an increased interatomic spacing tends to decrease the potential seen by the electrons in the material, which in turn reduces the band gap energy. The band gap value is higher when compared to the bulk value (1.7 eV). This blue shift could be attributed to the quantum confinement effect. This is basically due to the fact that the films deposited at low temperature give raise to smaller nanocrystallite size. The occurrence of small crystallite size indicates the presence of an increasing amount of amorphous phase mixed with the nanocrystalline phase [25].

3.2.2. Photoluminescence studies

Photoluminescence is a contactless, nondestructive method of probing the electronic structure of materials. The photoluminescence process is probably a charge transfer process, since the photoluminescence emission associated with the combination of the electrons from the conduction band and the holes in the valence band, the change of the near-band-edge [26,27]. We can obtain the energy gap from the photoluminescence spectra directly using the relation $E_g = h\nu$. From the Fig. 6 the photon energy of the 598 nm corresponds to 2.07 eV, which apparently gives rise to a direct transition; the photoluminescence band should show red shifts with increasing particle size after annealing at higher temperature. The emission at 679 nm corresponds to 1.82 eV. These results indicate that the band gap of semicounductor nanocrystalline thin films decreases with annealing temperature and increase in particle size. The reason is that with increasing annealing temperature, the grain size becomes larger and the ratio of surface area to volume decreases, correspondingly the defect density reduces. The decrease in peak intensity may be attributed to lattice deformation produced due to displacement of atoms in the annealing process [27]. These as-prepared and annealed nanocrystalline thin films represent a series of best emitters that are highly efficient, highly pure in emission and continuously tunable by simply varying the

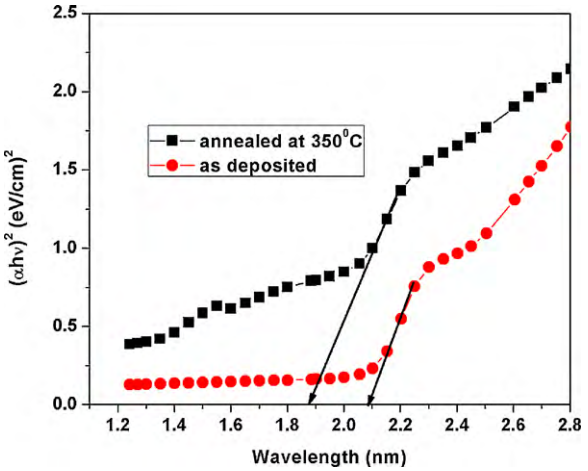

Fig. 5. Plot of $h\nu$ vs $(\alpha h\nu)^2$ for as-deposited and annealed CdSe thin films.

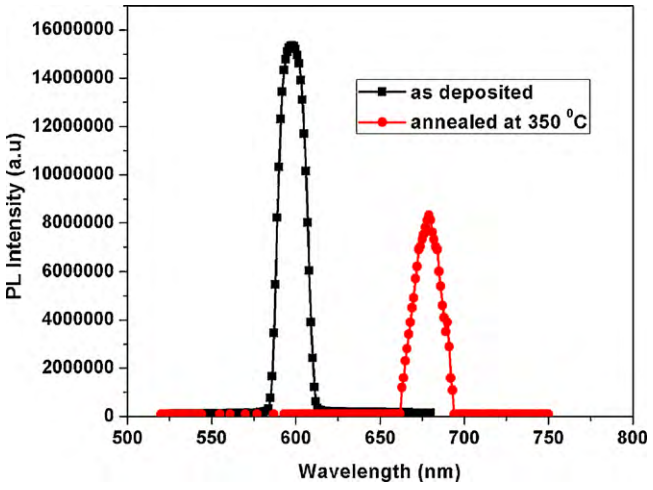

Fig. 6. Photoluminescence spectra of as-deposited and annealed thin films.

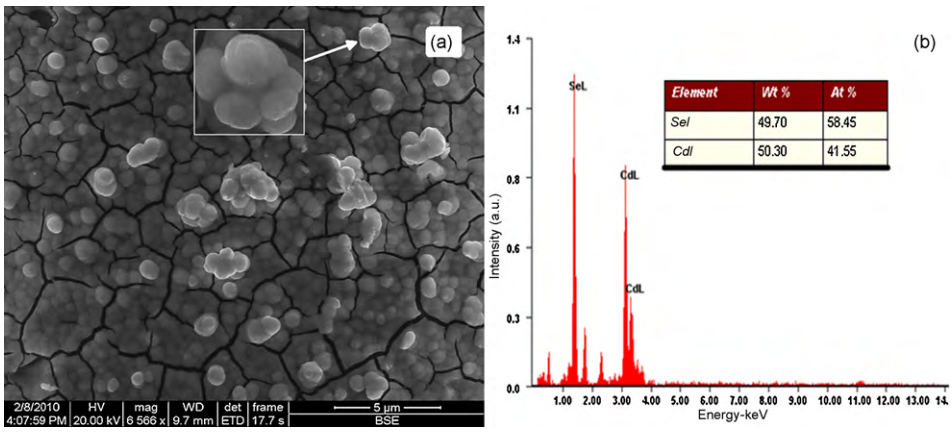

Fig. 7. (a) SEM photograph showing the micrograph of as-deposited CdSe thin film, (b) EDAX spectrum of as deposited CdSe thin film.

size of the nanocrystallites. These films are found to exhibit size dependent photoluminescence properties in the visible and ultraviolet region such that blue shifts are observed relative to the bulk value with decreasing particle size.

3.3. Surface morphology

High resolution scanning electron microscope is very helpful to study the surface morphology of films. Hence high resolution scanning electron microscope (HRSEM) investigation was performed using FEI Quanta 200 F model to scan the surface of the film. Fig. 7(a) shows the SEM image of the as deposited CdSe thin film. It can be observed that CdSe thin films are uniform, homogeneous and spreaded on the substrates. The SEM micrograph shows the compact polycrystalline surface composed of a single type of small, densely packed nanosized grains uniformly distributed over smooth homogeneous background. The quantitative compositional analysis of the CdSe film made using energy dispersive X-ray analysis (EDAX) is shown in Fig. 7(b). The composition of CdSe thin film is found to be approximately 1:1. The chemical bath deposited CdSe thin film is found to be good in stoichiometric nature. Inserted image shows the ball like particle gets agglomerated in the surface of the substrate. Fig. 8(a) shows the surface morphology of the annealed thin films. The ball like particle rearranges into pyramidal like structure when the as deposited samples annealed at 350 °C. Fig. 8(b) shows the energy dispersive X-ray analysis of annealed CdSe thin film. A small amount of compositional variation is observed in the annealed CdSe thin film, owing to the rearrangement of atoms. Inserted image shows the high magnification view of the pyramidal shape particles.

The surface morphology of the film was analyzed by atomic force microscopy. Fig. 9(a) and (b) shows the atomic force microscope image of the as-deposited and annealed CdSe thin films grown by chemical bath deposition technique on the glass substrate. It is observed from the surface image that the particles are uniformly distributed on the surface of the film. The atomic force microscopy image of 350 °C annealed CdSe film shows the agglomeration of particles in the film. These results are in good agreement with the SEM micrograph.

3.4. Electrical properties

The electrical properties of the materials are of great importance in determining the usage of the film for photovoltaic applications. The electrical property depends on various growth parameters such as film composition, thickness, deposition rate and substrate temperature [28]. For photovoltaics, the important characterization includes electrical conductivity and the interface behavior of the semiconductor with various metals. Hall effect measurements were carried out at room temperature to determine the carrier concentration, mobility, resistivity and conductivity of chemically deposited CdSe thin films using ECOPIA Hall effect measurement system. The as-deposited and annealed CdSe films have negative Hall coefficient which confirms, n-type conductivity. The Hall mobility of the as deposited CdSe film is found to be 0.2154 $cm^2/V\,s$, resistivity ($2.023 \times 10^7\ \Omega\,cm$), carrier concentration ($\eta = 1.223 \times 10^{12}/cm^3$) and conductivity ($7.308 \times 10^{-7}/\Omega\,cm$). The Hall mobility of the annealed CdSe film is found to be ($3.3 \times 10^3\ cm^2/V\,s$), resistivity ($8.21 \times 10^4\ \Omega\,cm$), carrier concentra-

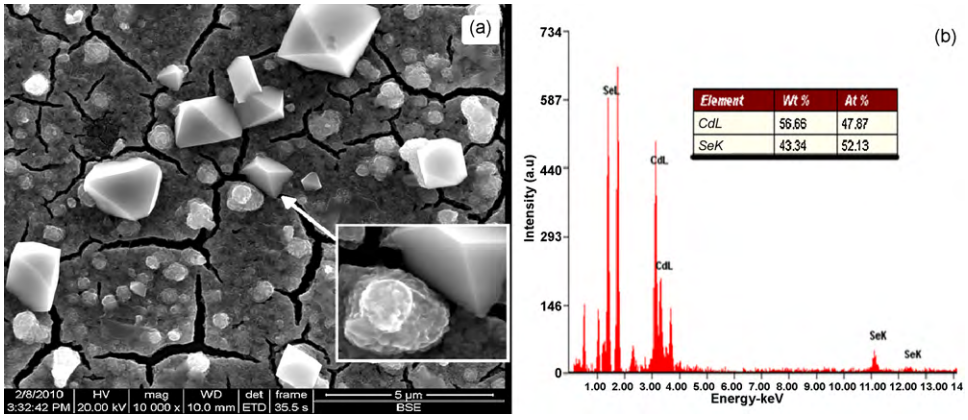

Fig. 8. (a) SEM photograph showing the micrograph of annealed CdSe thin film, (b) EDAX spectrum of annealed CdSe thin film.

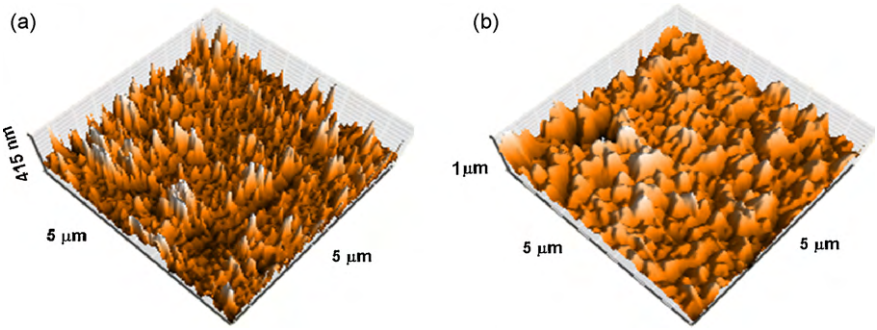

Fig. 9. (a) AFM image of as-deposited CdSe thin film (b) annealed CdSe thin film.

tion ($2.356 \times 10^{10}/cm^3$) and conductivity ($1.21 \times 10^{-5}/\Omega\,cm$). The electrical properties of the 350 °C annealed CdSe film get improved which show the decrease in the resistivity and increase in conductivity of the film.

4. Conclusions

In this article the importance of chemical bath deposition and the structural properties of CdSe thin films for various concentration of the EDTA are discussed. EDTA is used as a chelating agent to deposit CdSe films. By the addition of EDTA in solutions (metal ions), growth rate of film can be controlled which assist the uniform deposition of film. The thickness of the film is found to be 0.6 μm using interferometery technique. The as-deposited film exhibits the cubic structure and the 350 °C annealed film changes from cubic to hexagonal. Annealing of the film increases the crystallite size and decreases the dislocation density. The optical study reveals the direct transition band gap for as-deposited CdSe thin film and is found to be 2.1 and 1.84 eV for annealed film. The optical transmittance of the film gets reduced after annealing at 350 °C. From the photoluminescence analysis, it is inferred that the deposited samples have direct band transition and also red shift is observed after annealing. This shows CdSe is a potential candidate for solar cell fabrication. The homogeneous formations of crystalline grains were observed from SEM as well as AFM images. The as-deposited and annealed CdSe films have negative Hall coefficient which confirms the n-type conductivity. The Hall mobility of the material, resistivity, carrier concentration and conductivity were also estimated. Hence it is concluded that chemical bath deposition is a suitable method for the preparation of alloys and various metal chalcogenide thin films.

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