

Characterization of CdSe films prepared by chemical bath deposition method

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The optical, structural and electrical properties of Cadmium Selenide (CdSe) thin films were deposited by a simple and inexpensive method, chemical bath deposition (CBD), have been investigated. The optical measurements have been obtained by using the UV-Visible spectrophotometer and the optical band gap energy (E_g) was calculated from the absorption spectra as 1.83 eV and 1.76 eV for the chemically deposited CdSe thin films at 60 °C and 70 °C, respectively. The samples were characterized by using the X-ray diffraction method, the scanning electron microscope (SEM) and the energy dispersive X-ray analysis (EDX). The grain size of the films depend on the annealing temperature and is situated in the range 86 - 820 Å from X-ray analysis. The electrical resistivity and conductivity of the CdSe films have been determined by using four-point probe technique in the temperature range between 310–640 K. The electrical resistivities were found in the order of $10^5 \Omega\text{-cm}$ at room temperature and in order of $10^4 \Omega\text{-cm}$ at 640 K. The activation energy was found to be about 0.27 eV - 0.41 eV and the temperature coefficient of electrical resistivity was found to be about $-3.04 \times 10^{-3} \text{ K}^{-1}$ and $-3.27 \times 10^{-3} \text{ K}^{-1}$ for room temperature and 640 K, respectively.

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1. Introduction

The II-VI group compound (CdSe, ZnSe, CdS, CdTe etc.) are important because of their photovoltaic, photoelectrochemical (PEC) and electroluminescent applications and have received much attention [1-4]. The nanocrystalline semiconductor belongs 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. CdSe is a widely used $A^{II}B^{VI}$ group semiconductor whose band gap ($E_g=1.7$ eV) lies in the solar energy spectrum [5, 6]. It has a suitable band gap, a high absorption coefficient and high photosensitivity. Also, CdSe, along with some additives in it, forms an important class of semiconductor material, which finds applications in low cost devices such as light emitting diodes, solar cells, photodetectors, electrophotography and lasers [7-12]. CdSe thin films have been prepared by a number of vacuum and non-vacuum film deposition methods [13], including vacuum evaporation and co-evaporation [14], molecular beam deposition [15], laser ablation [16], electrochemical deposition [17], spray pyrolysis [18] and chemical bath deposition [1,5,19]. Compared to other methods, it is uniquely suited for deposition of a uniform film over large substrates of complex geometries. The substrates need not be conductive have a high melting point, or be combustion resistant. Film formation is truly a deposition of compound rather than a codeposition of separate elements. The chemical bath deposition is a low technology process,

requiring no high vacuum, high power supply or expensive equipment. The use of chemically deposited semiconductor films to develop photoelectrochemical solar cells or sensors was of basic interest in technological applications, most importantly, in the case of CdS and CdSe thin films [20-21].

The properties of materials prepared by the chemical bath deposition (CBD) method critically depend 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 H_2 , N_2 , Ar etc. [5]. The chemical bath deposition technique is well suited for producing large-area thin films for solar energy related applications [1].

The purpose of this study is to investigate optical, crystallographic properties, electrical resistivity and conductivity of chemically deposited CdSe thin films. We present the deposition method conditions in section 2.1; optical properties in section 2.2; X-ray diffraction, stoichiometric data in section 2.3; finally, the temperature coefficient of electrical resistivity and the activation energy are presented.

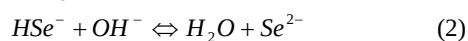
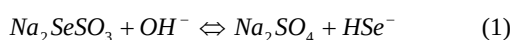
2. Experimental details

2.1. The deposition of CdSe thin films

The CdSe thin films were deposited on glass substrates by the chemical bath deposition. Commercially available glass slides (with a size of 75mm x 25mm x 2mm) washed with detergent and rinsed with deionized

water followed by rinsing in propanol and ethanol were used as substrates to deposit thin films. The clean glass slides were placed vertically on the walls of the 100 ml beaker containing the deposition mixture. After the deposition, the CdSe films were washed with propanol to remove the loosely adhered CdSe particles on the film and finally dried in air. A moderately stable Sodium Selenosulphate (Na_2SeSO_3), prepared by following the procedure reported earlier was used as a source of Se^{2-} ions [23]. The formation mechanism of the thin films can be described as follows:

Sodium selenosulphate (Na_2SeSO_3) in alkaline solution gives Se^{2-} ions as



In the presence of Cd^{2+} ions in the solution, CdSe is formed if the ionic product of Cd^{2+} and Se^{2-} exceeds the solubility of CdSe.

The mechanism of chemical deposition at low temperature is essentially based on the slow release of free Cd^{2+} to give CdSe. The CdSe formed homogeneously throughout the solution grows into clusters where they aggregate into layers. At higher temperatures, the thermal dislocation of the complex and anion is increased and the rate of release of selenium from sodium selenosulphate is more and growth of cluster occurs [24].

The stock solution of this reactive was prepared as follows: 12.5 g sodium sulfite and 4 g of selenium power were introduced into a 250 ml conical flask containing 100 ml of de-ionized water. The mixture was prepared at 90°C for 6h. A 100 ml chemical bath for the deposition of the CdSe films was prepared by the addition of the following: 3 ml of 1 M Cadmium Nitrate, 4 ml of 1 M TEA, 2.5 ml of %25 ammonia solution, 3 g of sodium sulfite, 7 ml of selenosulfate and deionized water. Glass slides were immersed and heated for various time and temperature range and then cooled to room temperature. The slides were removed and dried. A reddish thin film was formed on the substrates. The film thickness was increased by repeating the number of deposition. Rapid dark reddish precipitation in the solution took place with increase in the bath temperature. This might be due to the increased rate of release of selenium from sodium selenosulphate. As-deposited films were uniform and adhered well to the substrates.

In order to obtain CdSe thin films, they were first deposited on glass substrates by the chemical bath deposition at 60 °C for two hours and 70 °C for one hour. This process was repeated six times to increase the thickness. The solution was refreshed after every two hours for 60 °C and one hour for 70 °C, during the deposition. The thickness of the films was found to be 1.0 μm and 0.75 μm at 60 °C and 70 °C, respectively.

2.2 Optical properties

The optical properties of the CdSe films were measured by using UV-Visible spectrophotometer (SHIMADZU UV-1700) at room temperature in the wavelength range 190-1100 nm. The value of the optical band gap energy (E_g) was determined from the absorption spectra of the films by using the following relation [25]:

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

where A is a constant, $h\nu$ is the photon energy and n is a constant, equal to 1/2 for direct band gap semiconductor. The estimated band gap energy values were obtained from the curves of α^2 versus $h\nu$. The linear nature of the curves indicates the existence of the direct transition. The energy band gap was determined by extrapolating the straight portion to the energy axis at $\alpha = 0$.

2.3 Characterization of the CdSe thin films

The CdSe films with 1.0 μm thicknesses were produced for X-ray analysis at 60 °C. These films were annealed in air atmosphere at the temperatures of 373, 473, 573 and 673 K. The annealing time was one hour. The X-ray powder diffraction data was obtained by a Phillips diffractometer with the following settings: nickel filter, 40 kV at 30 mA, $\text{CuK}_{\alpha 1}$ line $\lambda = 1.5406 \text{ \AA}$. The microstructures of the two different samples were characterized using an LEO scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) spectrometers as well as a computer controlled image analyzer. After the electrical measurements, the chemical compositions of the samples were determined by using the EDX spectrometer with the possible error up to 1%. The CdSe thin films which have been used for the electrical measurements were prepared at 60 °C and at 70 °C, named as CdSe-60 °C and CdSe-70 °C.

2.4 Electrical measurements

The four-point probe method is the most widely used technique for electrical profile measurement of the materials. Two of the probes are used to source current and the other two probes are used to measure voltage, using four probes eliminates measurement errors due to the probe resistance, the spreading resistance under each probe, and the contact resistance between each metal probe and material [22].

The electrical measurements of the samples were obtained by DC four-point probe technique. A Keithley 2400 sourcemeter was used to provide the constant current and the potential drop was measured by a Keithley 2700 multimeter through interface card, which are controlled by a computer. Platinum wires with diameter of 0.5 mm were used as current and potential probes. The voltage drop was detected and the electrical resistivity and conductivity

were determined using a standard conversion method. The measurements have been made in the temperature range 310-640 K. The temperature of the sample has been changed by controllable Nabertherm type P 320 heater and the temperature of sample was measured using a standard K type thermocouple which was placed near the samples.

3. Results and discussion

3.1 Optical properties

The optical properties of the CdSe films were measured by using UV-visible spectrophotometer (SHIMADZU UV-1700) at room temperature in the wavelength range 190-1100 nm. The spectral distributions of transmittance of the films were determined and the thickness of the films were calculated from the transmission interference using equation

$$d = \frac{1}{2n \left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right)} \quad (4)$$

where d is the film thickness, n is refractive index, and λ_1 and λ_2 are adjacent maxima or minima of the transmission patterns [25].

The optical properties of the films deposited on glass substrate were determined from transmission measurement in the range 350-1100 nm. Fig. 1 and Fig. 2 show the variation of percentage transmission (%T) with wavelength, the variation of the absorption coefficient, α^2 , with energy, $h\nu$, respectively.

Fig. 1 shows the transmission spectra of the thin films deposited at 60 °C and at 70 °C. The optical transmittance value decreases with film thickness, which shows the improvement in crystallinity. From the transmission spectra the absorption coefficient (α) was calculated using the relation

$$\alpha = -\frac{\ln(T)}{d} \quad (5)$$

where T is transmittance. The calculated α^2 coefficients are found to be in the order of 10^9 cm^{-2} for the different thicknesses CdSe thin films. Fig. 2 shows a plot of α^2 versus energy $h\nu$. The linear dependence of the plots indicates that the types of transition in the films are direct. The direct band gap energies were estimated by finding the energy axis intercepts. The band gap energy was determined as 1.83 eV and 1.76 eV for the chemically deposited CdSe thin films at 60° C and 70 °C, respectively, which are in good agreement with earlier reports [26, 27].

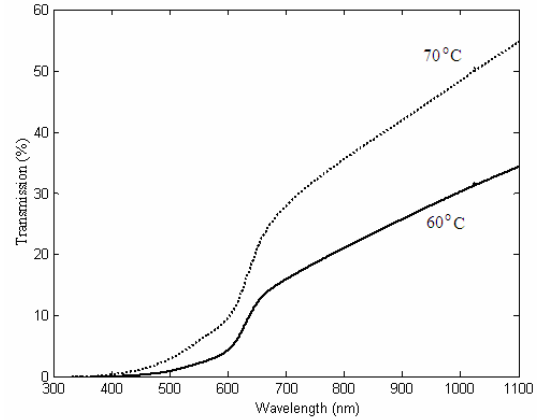


Fig. 1. The optical transmittance spectrum of CdSe films deposited at 60 °C and 70 °C .

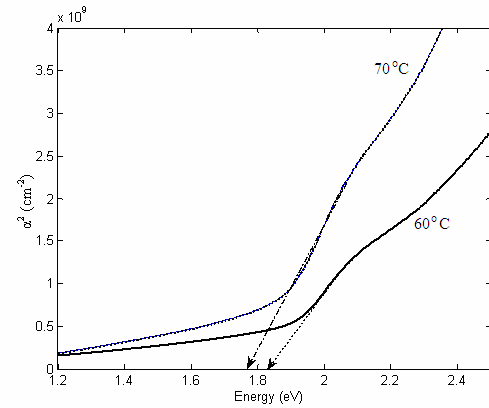


Fig. 2. The α^2 versus $h\nu$ graphs of CdSe films deposited at 60 °C and 70 °C.

3.2 Structural properties

The crystalline quality and orientation of the CdSe thin films have been investigated by means of X-ray diffraction. Fig. 3 shows the angular position, of five representative films of the signal intensities at $2\theta = \{25.54, 42.20, 49.92\}$, which indicates a cubic (Zincblende) structure for the as-grown samples according to JCPDS data files. The low intensity peaks show that the as-deposited CdSe thin films are include nanocrystallines. The thin film annealed at 373 K showed a structure of nanocrystalline cubic with slight improvement in crystallinity, whereas the film annealed at 573 K becomes polycrystalline with cubic structure. Further, the CdSe thin film annealed at 673 K was polycrystalline with a mixture cubic and hexagonal structure. Such a phase transition (from cubic to hexagonal) may occur due to change in atomic configuration, since smaller crystallite size and larger surface area seem to favor the phase transformation. The structural phase transformation from cubic to hexagonal has been reported [27, 28].

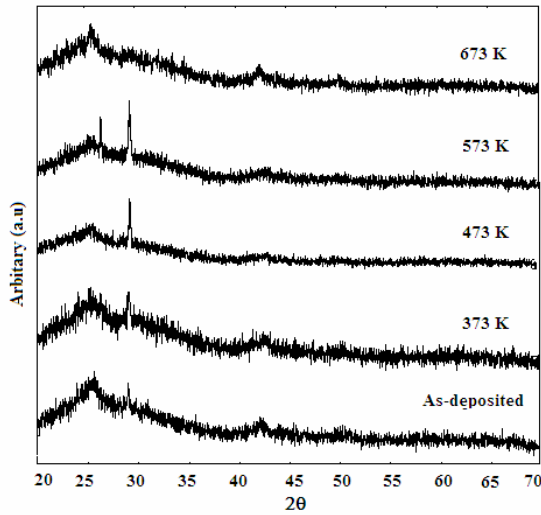


Fig. 3. X-ray diffraction data of CdSe films annealed in air at different temperatures.

Cadmium selenide can be formed with hexagonal, wurtzite-type structure or the cubic, zinc blende-type structure [29]. Previous workers reported that chemically deposited CdSe thin films onto the glass substrate are either hexagonal [24] or cubic [27, 30-32]. The identification and assignments of the observed diffraction patterns were made using the JCPDS data and by comparison with the published results. Since the X-ray diffraction graphs scaled down to A4 size and all of four graphs given as one figure many of their features are lost in this process, so all of the patterns observed are given in the Table 1 in detail; with assignments, d-spacing, observation angles (2θ) and full width at half maximum (FWHM) values. The data were obtained from the position of different peaks and using the Bragg law:

$$n\lambda = 2d \sin \theta \quad (6)$$

where θ is the angle of incidence, λ the wavelength of the incident X-rays, n is the order of the diffraction, and d is the distance between crystal planes.

The crystal sizes were determined from X-ray diffraction data. We use the standard (111) C reflection at $2\theta=25.54^\circ$. The FWHM values were seen to increase as the annealing temperature increase. The Scherrer formula,

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta} \quad (7)$$

where K is a constant, β is FWHM in radians, was used for the calculation of the crystallite sizes. The crystallite size for as- grown samples were found to be around 86 in the

fresh films and increases up to 820 Å by annealing, K value is taken as 0.9 for the calculations.

Table 1. X-ray diffraction data summary of 1 μ m CdSe films grown at 60 $^\circ$ C. (H: Hexagonal, C: Cubic).

Sample	Angle (2θ)	d (Å)	Width FWHM		Assignments
As-deposited	25.539	3.4850	0.941	CdSe	(111)C
	29.539	3.0216	0.375	Se	(101)H
	42.200	2.1397	0.100	CdSe	(220)C
	49.924	1.8253	0.367	CdSe	(311)C
Annealed at 373 K	25.440	3.4984	0.100	CdSe	(111)C
	29.498	3.0257	0.247	Se	(101)H
	42.020	2.1485	0.100	CdSe	(220)C
	49.700	1.8330	0.100	CdSe	(311)C
Annealed at 473 K	25.218	3.5286	0.753	CdSe	(111)C
	29.559	3.0196	0.196	Se	(101)H
	41.960	2.1514	0.100	CdSe	(220)C
	49.800	1.8295	0.100	CdSe	(311)C
Annealed at 573 K	25.40	3.5038	0.806	CdSe	(111)C
	29.52	3.0235	0.232	Se	(101)H
	42.48	2.1263	0.100	CdSe	(220)C
	49.80	1.8295	0.100	CdSe	(311)C
Annealed at 673 K	25.28	3.5201	0.100	CdSe	(111)C (002)H
	29.67	3.0080	0.824	Se	(101)H
	42.34	2.1329	0.457	CdSe	(220)C (110)H
	49.77	1.8303	0.817	CdSe	(311)C (112)H

The surface morphology of the films was observed by the SEM images. Fig. 4(a)-(b) shows the SEM images of the samples which do not have any impurities, porosities and structural defects. The morphology, the grain structure and the characteristics of surface were similar in the CdSe samples which were deposited at different temperature. From the micrographs, it is also observed that the films were homogeneous, without cracks or holes and they covered the glass substrate well. Fig. 4(a)-(b) shows the small spherical nanosized grains which indicate the nanocrystalline nature of CdSe films. Also, some overgrowths of particles were observed at few places.

In addition, the quantitative analysis of the films, which were grown on a glass substrate, was carried out by using the EDX analysis. This is shown in Fig. 5(a)-(b). The results of the EDX analysis show a typical EDX pattern and details of relative analysis for the films. The peaks of Cd and Se were clearly seen and the percentage of the element composition proved to be similar to the composition before the electrical measurements.

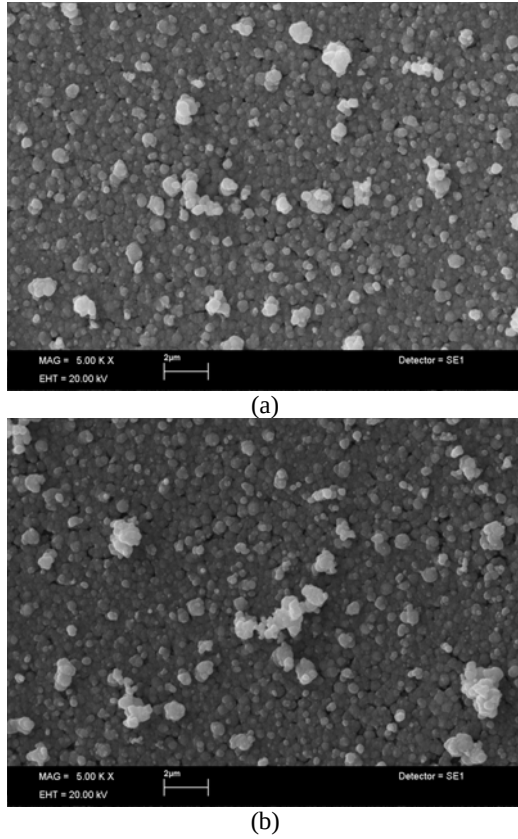


Fig. 4. The SEM micrographs of CdSe films grown a) at 60 °C and b) at 70 °C..

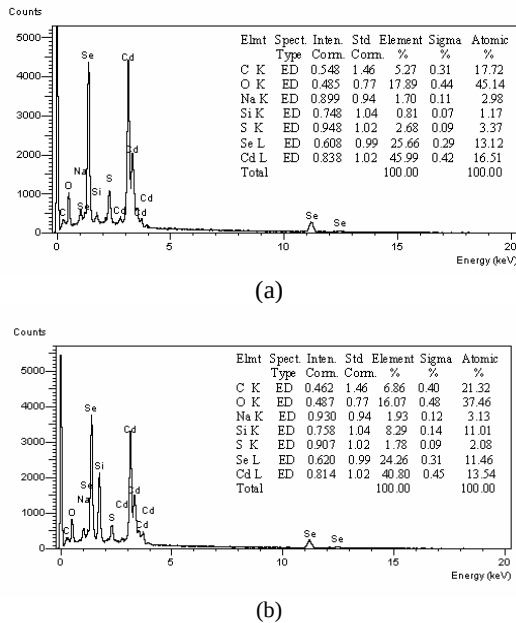


Fig. 5. The EDX analysis of CdSe films grown a) at 60 °C and b) at 70 °C..

3.3 Electrical resistivity and conductivity

The temperature dependence of electrical resistivity of the samples was shown in Fig. 6. The room temperature resistivities of the thin films were high of the order of $7.0 \times 10^6 \Omega\text{-cm}$ and agree with the published value of $6.0 \times 10^6 \Omega\text{ cm}$ [7]. The electrical measurement results show that the electrical resistivity of the samples decreases with temperature down to $3.0 \times 10^4 \Omega\text{ cm}$ at 640 K. Electrical measurement results indicate that the samples show typical semiconductor characteristics.

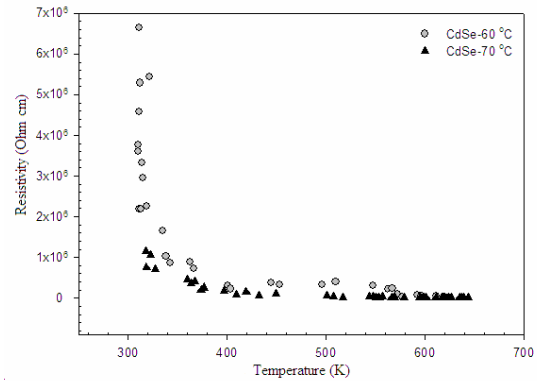


Fig. 6. Temperature dependence of the resistivity of CdSe thin films.

It is well known that thermal excitation can promote an electron into the conduction band of a semiconductor. Both electron and the accompanying hole are mobile thereby leading to electrical conductivity. It is also known that, the electronic transport properties of the polycrystalline semiconductors films are strongly influenced by their purity and structural characteristics such as grain size and boundaries, lattice defects, crystallite shape, impurities etc. The high resistivity of the thin films could be attributed to lattice defects and dislocations developed in the thin films prepared by chemical deposition method [5, 33-36].

The room temperature resistivity was found to be about $7 \times 10^6 \Omega\text{ cm}$. The high value of the room temperature resistivity can be attributed to the dislocations and imperfections of the films. The electrical resistivity of the chemically deposited CdSe films was used for calculating the activation energy. The activation energy of dark resistivity can be found by using the relation of

$$\rho = \rho_0 \exp(E_a / kT) \quad (8)$$

and plotting $\ln(\rho / \rho_0)$ versus $1000/T$, where ρ is the electrical resistivity at temperature T , ρ_0 is the resistivity at room temperature, k is the Boltzmann constant and E_a is the activation energy. Fig. 8 shows the plot of $\ln(\rho / \rho_0)$ versus $1000/T$ (K^{-1}). The activation energies are found from the slopes of two different region of Fig. 7. The E_a are found about 0.28 eV and 0.27 eV in the low temperature region (LR) and 0.41 eV and 0.35 eV in the high

temperature region (HR) for two different samples. These values show that Fermi energy is above the $(E_g/2)$ level.

The relative low activation energy (under $T=500$ K) can be related not only to the Fermi level energy but a part of it could reflect the height of potential barriers between the grains.

In addition, the temperature coefficient of electrical resistivity (TCR) for the CdSe films was also estimated by using the following equation [37],

$$\alpha_{TCR} = \left(\frac{1}{\rho_1}\right)\left(\frac{\partial \rho}{\partial T}\right) = \left(\frac{1}{\rho_1}\right)\left(\frac{\Delta \rho}{\Delta T}\right) \quad (9)$$

Table 2. Electrical resistivity, electrical conductivity, activation energy and temperature coefficient of electrical resistivity of the CdSe thin films.

Sample/T	Band gap E_g (eV)	Resistivity ρ (Ω cm)		Conductivity σ (Ω cm) $^{-1}$		Activation energy E_a (eV)		Temperature coefficient of resistivity α_{TCR} ($\times 10^{-3}$ K $^{-1}$)
		315 K	600 K	315 K	600 K	LR	HR	
CdSe (60 °C)	1.93	2.25×10^6	4.17×10^4	4.45×10^{-7}	2.39×10^{-5}	0.28	0.41	-3.27
CdSe (70 °C)	1.80	1.15×10^6	8.13×10^4	1.72×10^{-7}	2.45×10^{-5}	0.27	0.35	-3.04

LR: Low temperature region and HR: High temperature region

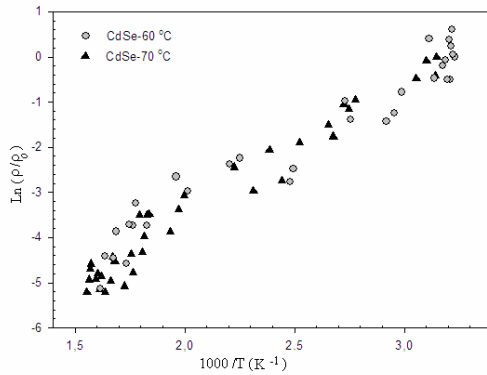


Fig. 7. Plot of $\ln(\rho/\rho_0)$ versus inverse temperature for CdSe thin films.

4. Conclusions

In summary, the optical, structural and electrical properties of the CdSe thin films which are grown by the CBD method have been investigated. The thickness and the optical band gap were found to be 1.0 and 0.75, 1.83 and 1.76 eV at 60 °C and 70 °C, respectively. These values are in agreement with the literature [24, 27].

The X-ray diffraction results of the samples show that there is a phase transition from the cubic structure to the hexagonal structure at higher temperatures (above 573 K). The grain size of the films were increased from 86 nm to 820 Å with the increasing annealing temperature. Surface morphology of the films shows that small spherical nanosized grains exist which indicates the nanocrystalline nature of CdSe.

where α_{TCR} is the temperature coefficient of electrical resistivity in the temperature between $\Delta T = T_2 - T_1$.

$\Delta \rho = \rho_2 - \rho_1$, ρ_1 is the electrical resistivity at T_1 and ρ_2 is the electrical resistivity at T_2 . The TCR of the CdSe films are calculated in the temperature range 310-640 K, which were found to be -3.04×10^{-3} K $^{-1}$ and -3.27×10^{-3} K $^{-1}$.

Some typical values of the band gap energy, electrical resistivity, electrical conductivity, and activation energy and temperature coefficient of electrical resistivity for the CdSe thin films are given in the Table 2.

In addition, the electrical resistivity values vary between 7×10^6 Ω -cm – 3×10^4 Ω -cm with the increasing temperature. The activation energies of the films were calculated. They have values in the range 0.27 eV – 0.41 eV for two different samples. Also, the temperature coefficients of electrical resistivity were found around -3.04×10^{-3} and -3.27×10^{-3} .

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References

- [1] K. R. Murali, V. Swaminathan, D. C. Triverdi, Solar Energy Mater. and Solar Cells **113**, 81 (2004).
- [2] D. Hahn, K. K. Mishra, K. K. Rajeshwar, J. Electrochem. Soc. **100**, 138 (1991).
- [3] K. K. Mishra, K. K. Rajeshwar, J. Electroanal. Chem. **273**, 169 (1989).
- [4] K. R. Murali V. Subramanian, N. Ransgarajan, A. S. Laskshmanan, S. K. Rangarajan, J. Electroanal. Chem. **368**, 95 (1994).
- [5] R. B. Kale, C. D. Lokande, Semicond. Sci. Techol. **1** 20 (2005).
- [6] S. J. Lade, M. D. Uplane, C. D. Lokhande, Mater. Chem. Phys. **36** 68 (2001).

- [7] P. P. Hankare, S. D. Delekar, P. A. Chate, S. D. Sabane, K. M. Garadkar, V. M. Bhuse, *Semicond. Sci. Technol.* **70**, 19 (2004).
- [8] D. Haneman, G. H. Wentenaar, R. C. Kainthla, *Solar Energy Mater.* **69**, 10 (1984).
- [9] A. Ya, E. T. B. Afuzov, Afuzov, V. M. Sviriuv, *Galiotekhnika*, **69**, 4 (1984).
- [10] A. K. Rautri, R. Thangraj, A. K. Sharma, B. B. Tripathi, O. P. Agnivotri, *Thin Solid Films* **55**, 91 (1982).
- [11] S. Uthana, P. J. Reddy, *Phys. Status Solidi A* **269**, 65 (1981).
- [12] M. Fuji, T. Kwai, O. Kawais, *Butsuri* **57**, 57 (1984).
- [13] T. Gruszeckix, B. Holmstrom, *Solar Energy Materials and Solar Cells* **227**, 31 (1993).
- [14] J. Reicman, M. A. Russak, *J. Appl. Phys.* **708**, 53 (1982).
- [15] M. Hyugaji, T. Miura, *Jpn. J. Appl. Phys.* **1575**, 24 (1985).
- [16] G. Perna, V. Capozzi, M. Ambrico, *J. Appl. Phys.* **3337**, 83 (1998).
- [17] K. C. Mandal, O. Savadogo, *J. Mater. Sci.* **4355**, 27 (1992).
- [18] C. J. Liu, J. H. Wang, *Appl. Phys. Lett.* **852**, 36 (1980).
- [19] R. A. Boudreau, D. R. Rauh, *J. Electrochem. Soc.* **513**, 130 (1983).
- [20] R. S. Mane, C. D. Lokhande, *Thin Solid Films* **56**, 304 (1997).
- [21] D. Nesheva, Z. Aneva, S. Reynolds, C. Main, A. G. Fitzgerald, *J. Optoelectron. Adv. Mater.* **8**(6), 2120 (2006).
- [22] L. Valdes, *Proc. I.R.E.*, 1954, p. 420.
- [23] M. E. Rincon, M. Sanchez, A. Olea, I. Ayala, P. K. Nair, *Solar Energy Mater. and Solar Cells* **399**, 52 (1998).
- [24] S. S. Kale, C. D. Lokhande, *Mater. Chem. Phys.* **103**, 62 (2000).
- [25] J. N. Pankove, *Optical Processes in Semiconductors*, Dover, New York (1971).
- [26] M. T. S. Nair, P. K. Nair, A. Zingaro, E. A. Meyers, *J. Appl. Phys.* **74**, 1879 (1993).
- [27] M. Dhanam, R. R. Prabhu, P. K. Manoj, *Mater. Chem. Phys.* **107**, 289 (2007).
- [28] O. Portillo-Moreno, R. Lozada-Morales, M. Rubin-Falfan, J. A. Perez-Alvarez, M. Rubin-Falfana, *J. of Phys. and Chem. of Solids* **1751**, 61 (2000).
- [29] JPDS Files No: 08-459 and 19-191
- [30] R. C. Kainthala, D. K. Pandaya, K. L. Chopra, *J. Electrochem. Soc.* **277**, 127 (1980).
- [31] G. Hodes, A. Albu-Yaran, F. Decker, P. Matsuke, *Phys. Rev. B* **4215**, 36 (1987).
- [32] R. B. Kale, C. D. Lokhande, *Applied Surface Science* **343**, 223 (2004).
- [33] K. L. Chopra, *Thin Film Phenomenon* (New York: McGraw-Hill), 1969.
- [34] G. Harbeke (ed), *Polycrystalline Semiconductors: Physical Properties and Applications* (Berlin: Springer), 1985.
- [35] G. I. Rusu, M. E. Popa, G. G. Rusu, I. Salaoru, *Appl. Surf. Sci.* **222**, 218 (2003).
- [36] R. S. Rusu, G. I. Rusu, *J. Optoelectron. Adv. Mater.* **7**(2) 823 (2005).
- [37] T. Gron et al., *Phys. Rev. B* **35208**, 71 (2005).

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