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# Structural, optical and electrical characterization of chemically deposited CdSe thin films

A.S. Khomane[a,*], P.P. Hankare[b]

[a] Department of Chemistry, Rajaram College, Kolhapur 416004, Maharashtra, India
[b] Department of Chemistry, Shivaji University, Kolhapur 416004, Maharashtra, India

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ABSTRACT

Cadmium selenide (CdSe) thin films have been deposited on glass substrate. CdSe thin films were characterized by various techniques such as X-ray diffraction, scanning electron microscopy and UV–vis–NIR double beam spectrophotometer. The electrical and thermo-electrical properties are also studied. The X-ray diffraction analysis shows that the film samples are in cubic crystal structure. The optical band gap energy (Eg) was found to be 1.7 eV.

## 1. Introduction

Cadmium selenide is a popular semi-conducting material from the II–VI group. It is used as thin film transistors, sensors, lasers, photoluminescence and optoelectronic devices in photoconductive and photovoltaic cells [1–14]. The nano-crystalline CdSe material is also used as photo-electrode in photo-electrochemical cell [15].

CdSe thin films can be deposited by various techniques such as vacuum evaporation [1,5,15], electro-deposition [16,17], spray pyrolysis [18,19], thermal evaporation [20], successive ionic layer adsorption and reaction (SILAR) [21] and chemical bath deposition (CBD) [22–24]. Among these methods chemical bath deposition (CBD) has greater advantages than others. Chemical bath deposition is quiet simple, does not require sophisticated instruments and large area deposition is possible. Therefore we have selected CBD method to synthesize CdSe material.

This paper deals with synthesis of cadmium selenide thin films by chemical bath deposition at room temperature. The materials obtained were characterized by X-ray diffraction, SEM and optical absorption. Besides this the electrical properties of CdSe films are also studied.

## 2. Experimental details

### 2.1. Synthesis of cadmium selenide thin film

For the deposition of CdSe thin films cadmium chloride and sodium seleno-sulphate were used as source of $Cd^{2+}$ and $Se^{2-}$ ions respectively. While the malonic acid is used as a complexing agent in the synthesis of CdSe thin films. The $Cd^{2+}$ ions form complex with malonic acid and give cadmium malonate. Cadmium malonate slowly releases $Cd^{2+}$ ions from the complex, which are used for the slow and uniform deposition of CdSe thin films. The sodium seleno-sulphate ($Na_2SeSO_3$) was obtained by refluxing selenium powder (5 g) with sodium sulphite (12 g) in 200 ml distilled water for several hours [25]. The non-conducting glass plates of dimensions 26 mm × 76 mm × 2 mm were used as a substrate. The glass substrates were washed in chromic acid and finally with distilled water before deposition of the film.

For the deposition of cadmium selenide thin films 10 ml 0.25 M $Cd^{2+}$ ions are complexed with malonic acid. Ammonia and sodium hydroxide are added to maintain the pH of the solution. Then above solution was diluted up to 50 ml with distilled water. Then 10 ml 0.25 M sodium seleno-sulphate was added in the above reaction mixture. Then glass substrates were kept in reaction mixture for 24 h at room temperature. The pH of reaction mixture was found to be 7.5. As the ionic product of $Cd^{2+}$ and $Se^{2-}$ ions exceeds the solubility product of CdSe, then deposition of CdSe thin films on glass substrates takes place.

After 24 h, the glass substrates were removed washed with distilled for several times and dried naturally preserved in a dark desiccator over anhydrous $CaCl_2$. Cadmium selenide films were found to be homogenous, well adherent to the glass substrate and orange red in color.

### 2.2. Characterization of film sample

CdSe thin films were characterized by using Phillips PW-1710 X-ray diffractometer in $2\theta$ range from 10° to 80° using Cr $K\alpha_1$ line (wavelength = 2.28970 Å).

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* Corresponding author. Tel.: +91 231 2537840; fax: +91 231 2531989.
*E-mail address:* ashok_khomane@rediffmail.com (A.S. Khomane).

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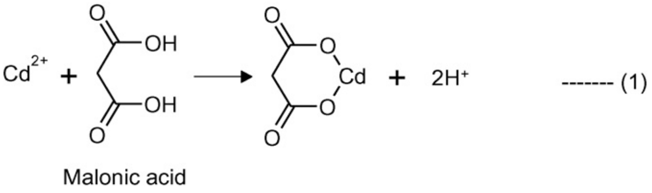
Cambridge Stereo Scan (USA) Scanning Electron Microscope (SEM) was used for surface morphological study. The optical absorption was recorded in the wavelength range from 400 to 1400 nm using UV–vis–NIR double beam spectrophotometer (Hitachi-330 Japan) at room temperature. The analysis of spectrum was done by computing the values of absorption at every step of 2 nm. The thickness of the film was estimated by weight difference density consideration technique. The electrical resistance measurements were carried out in temperature range 300–550 K on Zintek – 502 BC Milliohm meter using two-probe method. The thermo-electric power measurements were made by maintaining a temperature gradient along the length of the film and measuring, the potential difference across the terminals having a separation of 1 cm with the help of a digital microvolt meter.

## 3. Results and discussion

### 3.1. Growth mechanism

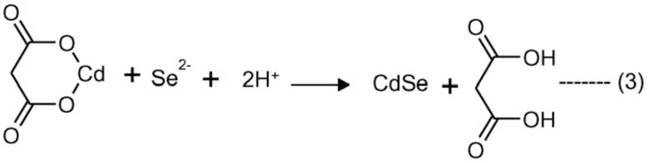
The proposed overall growth reaction mechanism of CdSe thin films is given below [26]:



(1)

$$Na_2SeSO_3 + 2\,^{-}OH \longrightarrow Se^{2-} + Na_2SO_3 + H_2O \quad \text{------- (2)}$$

(2)



(3)

The solubility product of CdSe is ($K_{sp}$ CdSe) = $10^{-33}$. As the ionic product of $Cd^{2+}$ and $Se^{2-}$ ions exceeds to solubility product of CdSe then deposition of CdSe film takes place. The color of the deposited CdSe film was found to be orange red in color.

### 3.2. Structural analysis

X-ray diffractograms of deposited CdSe thin film and annealed CdSe film at 450 °C are shown in Fig. 1. The observed *d*-values and respective prominent peaks correspond to the reflection from the (1 1 1), (2 2 0) and (3 1 1) planes, which coincide well with the JCPDS data [27]. The results of X-ray analysis well agree with earlier reported method [14,22–24,28–34]. From this it can be concluded that the deposited CdSe films are poly-crystalline in nature with cubic modification.

The lattice parameter '*a*' has been calculated by using following equation:

$$a = d\sqrt{h^2 + k^2 + l^2} \tag{4}$$

where '*d*' is the interplanar distance and '*h*, *k*, *l*' are the Miller indices of the lattice planes (Table 1).

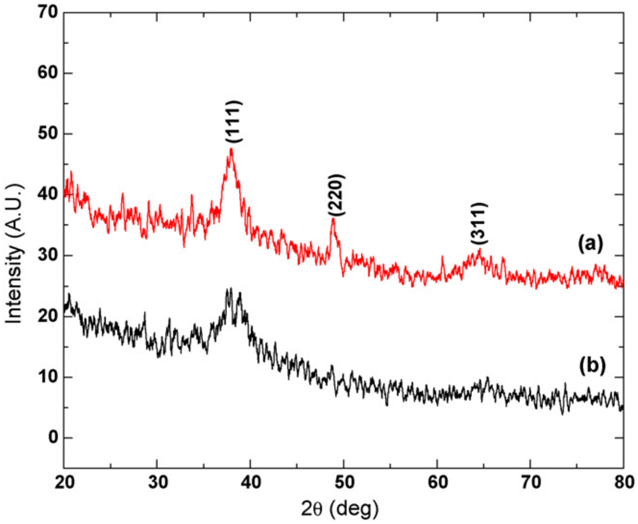


**Fig. 1.** (a) XRD-pattern of annealed CdSe thin film and (b) XRD-pattern of as deposited CdSe thin film.

The crystallite size ($D$) in the films has been evaluated by using Scherrer's formula:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{5}$$

where $K$ is constant (0.94), $\lambda$ is wavelength of the X-ray used, $\beta$ is broadening of diffraction line measured at half of its maximum intensity (in rad) and $\theta$ is Bragg's diffraction angle. The grain size of CdSe thin film was found to be 25–30 nm.

### 3.3. SEM studies

The scanning electron micrograph of annealed CdSe thin films at 450 °C is shown in Fig. 2. This technique is used to study the surface morphology of the film sample. The SEM micrograph of annealed CdSe thin films at 450 °C shows smooth and uniform surface without cracks and well adherent to the glass substrate. The annealed sample shows total conversion into nanorods [31].

### 3.4. Optical properties

The optical properties of the CdSe films were measured on UV–vis–NIR double beam spectrophotometer at room temperature in the wavelength range 400–1400 nm. A careful observation of the spectra revealed the presence of a broad absorption edge in the 600–800 nm range. Optical properties are studied by recording the transmittance of the films. Optical investigations of films revealed that there is band to band direct type of transitions. The broadening of an absorption edge is due to the grain boundary discontinuity and the disorderness developed in the material during film formation [25].

The band gap energy (Eg) was determined by plotting a graph of $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 3. The linear nature of plot indicates the existence of the direct transition. The band gap 'Eg' was determined by extra plotting the straight line to the energy

**Table 1**
Crystallographic parameter of CdSe thin film.

| Film composition | 'd' values in Å (JCPDS) | 'd' values observed | *h k l* planes | Cell parameters (Å) |
|---|---|---|---|---|
| CdSe | 3.5100 | 3.5045 | 1 1 1 | 6.0709 |
| | 2.1490 | 2.1465 | 2 2 0 | |
| | 1.8330 | 1.8307 | 3 1 1 | |

**Fig. 2.** SEM micrographs of annealed CdSe thin film at 450 °C.

axis whose intercept to the *x*-axis gives the optical band gap. The band gap of CdSe film was found to be 1.7 eV which agrees with earlier investigators report [11,14,22,25,35].

### 3.5. Electrical conductivity and transport properties

The electrical resistivity and conductivity of the sample were measured in the temperature range 300–550 K. The conductivity of sample increases with increase in temperature shows semiconducting behavior. The decreasing trend in the conductivity may be due to the increase in the crystallite size in the CdSe thin films. The plot of log $\sigma$ versus (1000/$T$) for the film is shown in Fig. 4. The non-linear nature of the plot indicates two types conduction mechanism, also explains the same. The electrical specific conductivity of the sample was found to be order of $10^{-6}\,(\Omega\,\mathrm{cm})^{-1}$. The activation energy is determined by using Arrhenius equation which can be given as [36]:

$$\sigma = \sigma_0 e^{-Ea/kT} \tag{6}$$

where $\sigma$ is measured electrical conductivity, $\sigma_0$ is the conductivity pre-exponential factor, $k$ is Boltzmann's constant and $T$ is absolute temperature. The '*Ea*' was found to be in the range between 0.640 eV in the high temperature region and 0.125 eV in the lower temperature region. The activation energy results were found in good agreement with the other investigator results [35,37]. In thermoelectric power measurements, the open circuit thermo voltage generated by the sample when a temperature gradient is applied across a length of the sample was measured using a potentiometer. From the sign of the potentiometer terminal connected at the cold end, one can deduce the sign of the predominant charge carriers. In our investigation of film sample, the negative terminal was connected to the cold; therefore film sample shows n-type of conductivity [22,35,37].

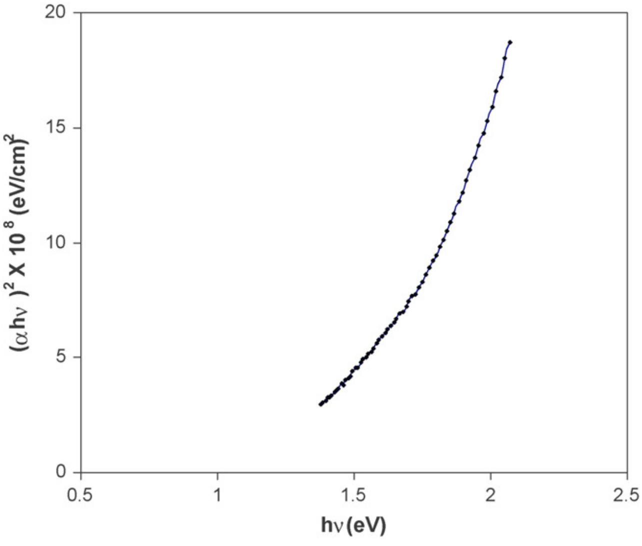


**Fig. 3.** Plot of $(\alpha h\nu)^2$ versus $h\nu$ of CdSe thin film.

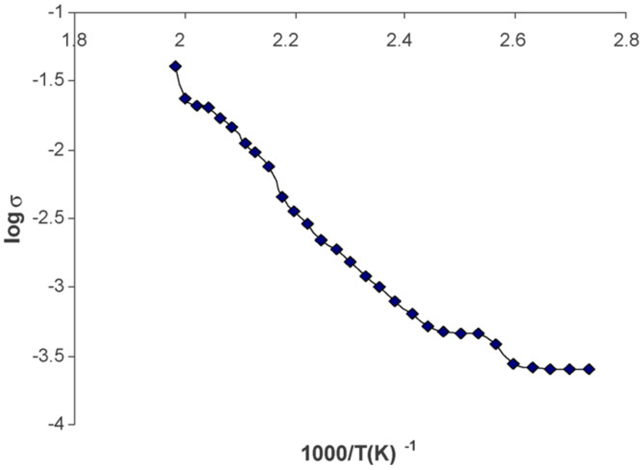


**Fig. 4.** Plot of log $\sigma$ versus (1000/$T$) of CdSe thin film.

## 4. Conclusions

- (i) Binary CdSe thin films can be deposited by modified CBD method at room temperature.
- (ii) XRD analysis reveals CdSe exhibit in cubic crystal structure.
- (iii) Optical studies revealed direct to direct type of transitions and band gap was found to be order of 1.7 eV.
- (iv) The specific conductance of CdSe sample was found to be order of $10^{-6}\,(\Omega\,\mathrm{cm})^{-1}$.
- (v) TEP measurement of the sample showed n-type of conduction mechanism.

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## References

[1] D.P. Padiyam, A. Marikani, K.R. Murali, Mater. Chem. Phys. 78 (2002) 51.
[2] M. Bouroshian, J. Charoud Got, Z. Loizos, N. Spyrellis, G. Maurin, Thin Solid Films 381 (2001) 39.
[3] K.C. Sathyalatha, S. Uthanna, P. Jayarama Reddy, Thin Solid Films 174 (1989) 233.
[4] D. Samantha, B. Samantha, A.K. Chudhuri, S. Ghorai, U. Pal, Semi-Cond. Sci. Technol. 11 (1996) 548.
[5] R.M. Abdel-Latif, Physica B 270 (1999) 366.
[6] T. Gruszecki, B. Holmstrom, Sol. Energy Mater. Sol. Cells 31 (1993) 227.
[7] A. Van Calster, A. Vervat, I. De Rycke, J. De Baets, J. Cryst. Growth 86 (1989) 924.
[8] G. Zou, H. Ju, Anal. Chem. 76 (23) (2004) 6871.
[9] R. Wang, H. Peter Jakobson, R. Kou, J. Tang, R.Z. Fineman, D. Yu, Y. Lu, Chem. Mater. 18 (18) (2006) 4231.
[10] J.W. Edmund, E.M. Dale, R.N. Donald, B.E. Arthur, F.G. John, T.F. Kucch, J. Cryst. Growth 148 (1995) 63.

[11] M. Dhanam, R.R. Prabhu, P.K. Manoj, Mater. Chem. Phys. 107 (2008) 289–296.
[12] M.A. Hernan dez-Perez, J. Aguilar Hernandez, G. Centreras-Puente, J.R. Vargas-Garcia, E. Rangel-Salinas, Phys. E: Low-Dimens. Syst. Nanostruct. 40 (2008) 2535–2539.
[13] S.M. Pawar, A.G. Moholkar, P.S. Shinde, K.Y. Rajpure, C.H. Bhosale, J. Alloys Compd. 459 (2008) 515–520.
[14] H.E. Esparza-Ponce, J. Hernandez-Borja, A. REyes-Rojas, M. Cervantes-Sanchez, Y.V. Vorbier, R. Ramirez-Bon, J.F. Perez-Robles, J. Gonzalez-Hernandez, Mater. Chem. Phys. 113 (2009) 824–828.
[15] K. Subba Ramaiah, Y.K. Su, S.J. Chang, F.S. Juang, K. Ohdaira, Y. Shiraki, H.P. Liu, I.J. Chen, A.K. Bhatnagar, J. Cryst. Growth 224 (2001) 74.
[16] C.D. Lokhande, E.H. Lee, K.D. Jung, O.S. Joo, Mater. Chem. Phys. 91 (2005) 399.
[17] S.M. Rashwan, S.M. Abdul-Wahab, M.M. Mohammed, J. Mater. Sci. Mater. Electron. 1818 (2007) 575.
[18] T. Elango, V. Subramanium, K.R. Murali, Surf. Coat. Technol. 123 (2000) 8.
[19] Yu.V. Melelera, N.A. Redy Chev, G.F. Nevikor, Inorg. Mater. 43 (5) (2007) 455.
[20] K.N. Shreekanthan, B.V. Rajendra, V.B. Kasturi, G.K. Shivakumar, Cryst. Res. Technol. 38 (1) (2003) 31.
[21] O. Yomamoto, T. Sasamoto, M. Inagaki, J. Mater. Res. 13 (1998) 3394.
[22] P.P. Hankare, S.D. Delekar, M.R. Asabe, P.A. Chate, V.M. Bhuse, A.S. Khomane, K.M. Garadkar, B.D. Sarwade, J. Phys. Chem. Solids 67 (2006) 2506–2511.
[23] P.D. More, G.S. Shahane, L.P. Deshmukh, P.N. Bhosale, Mater. Chem. Phys. 80 (2003) 48.
[24] R.C. Kainthila, D.K. Pandya, K.L. Chopra, J. Electron. Chem. Soc. (1980) 277.
[25] C.S. Shahane, D.S. Sutrve, L.P. Deshmukh, Ind. J. Pure Appl. Phys. 34 (1996) 153–157.
[26] F.I. Ezema, R.U. Osuji, Chalcogenide Lett. 4 (6) (2007) 69–75.
[27] JCPDS Data File No. 00-019-0191.
[28] P. Nemec, D. Mikes, J. Rohorec, E. Uhllirova, F. Trojanek, P. Maly, Mater. Sci. Eng. B 69–70 (2000) 500.
[29] G. Hodes, A.A. Yaran, F. Decker, P. Motisuke, Phys. Rev. B 36 (1987) 4215.
[30] S. Gorer, G. Hodes, J. Phys. Chem. 98 (1994) 5338.
[31] R.B. Kale, C.D. Lokhande, Semi-Cond. Sci. Technol. 20 (2005).
[32] M.E. Hernandez Torres, R.S. Gonzates, H.N. Contreras, M.A. Vidal, J.M. Gracia, Mod. Phys. Lett. B 15–19 (2001) 741.
[33] H. Padmanabha Sarma, N. Rangarajan, K.R. Murali, Phys. Status Solidi (a) 148 (1995), K77.
[34] S. Evat, H. Metin, M. Ari, Mater. Chem. Phys. III (2008) 114–120.
[35] P.P. Hankare, A.D. Jadhav, V.M. Bhuse, A.S. Khomane, K.M. Gradkar, Mater. Chem. Phys. 80 (2003) 102.
[36] K.J. Laidler, The World of Physical Chemistry, Oxford University Press, 1993.
[37] P.P. Hankare, V.M. Bhuse, K.M. Garadkar, S.D. Delekar, I.S. Mulla, Semicond. Sci. Technol. 19 (2004) 70–75.