Consequences of air annealing on structural, optical and refractive properties of CdSe thin films

V. J. Sawant, D. A. Lavate, A. S. Khomane[a*] [a]Department of Chemistry,
Government Rajaram College, S.U.Road, Vidyanagar, Kolhapur. Maharashtra 416 004, India.

Abstract

The CdSe thin films were successfully synthesized by simple chemical bath deposition method. The effective modification in structure and optical properties of CdSe thin films were observed due to controlled air annealing at elevated temperatures. The CdSe thin films were characterized by XRD and UV-vis-NIR techniques. As deposited CdSe sample shows amorphous nature of material. An annealed thin film sample shows phase transformation with respect to temperature. As deposited film sample shows energy band gap 1.7 eV while an annealed sample shows energy band gap 2.2 eV. Refractive index of as deposited CdSe thin film sample was found to be 2.71.

Keywords - Chemical bath deposition, XRD, UV-vis-NIR, Refractive index.

1.0 Introduction

Cadmium selenide is one of the interesting semi-conducting material due to its electrical, optical and refractive properties. Because of its lot of potential applications, it is widely used as a photo electrode, sensors, lasers, transistors, photoconductive and photovoltaic devices [1-3].

We have synthesized CdSe thin films by simple, economical and eco- friendly chemical bath deposition method [4]. The use of dichloroacetic acid during reaction progress increase the rate of formation of CdSe material to get uniform coating. The effect of air annealing on CdSe thin films were studied by XRD and UV-vis-NIR techniques.

2.0 Materials and Methods

For the synthesis of CdSe thin films the AR grade chemicals, such as cadmium carbonate, selenium black metal powder, dichloroacetic acid, sodium sulphite, ammonia and sodium hydroxide were used. In the synthesis of CdSe sample cadmium dichloro acetate was obtained by dissolving cadmium carbonate in the solution of dichloroacetic acid. Sodium seleno-sulphate (Na_2SeSO_3) was prepared by reflux action of selenium powder with sodium sulphite [5]. The glass plates of dimensions 75 x 26 x 2 mm were used for the deposition of CdSe thin film sample. The glass plates were washed in chromic acid, alcohol and distilled water before deposition of the film sample [6]

In the synthesis of CdSe thin film sample, 10 ml 0.25N solution of cadmium dichloro acetate was taken into 100ml capacity beaker. Very dilute solution of ammonia was added to precipitate cadmium hydroxide, and then precipitate of cadmium hydroxide was dissolved in excess of dilute ammonia. To this reaction mixture 10ml 0.25N sodium seleno-sulphate was added with constant stirring. After that the glass plates were kept in the reaction mixture for 24 hours at room temperature. The glass plates were removed from the beaker and washed with distilled water. The color of the successfully deposited CdSe sample on glass plate was found to be orange red [7]. The use of dichloro acetic acid during synthesis of CdSe sample increases the rate of reaction due to inductive effect of two electronegative Cl^- ions present in cadmium dichloro acetate.

The structural parameters of CdSe film sample were determined on Phillips PW-1710 X-ray diffractometer. CdSe film sample were scanned in the range of 25° to 85° as 2θ by using Cr $K\alpha_1$ (wavelength = 2.28970A°) The optical absorption analysis was done in the wavelength range of 400 to 800 nm by using double beam spectrophotometer at room temperature. The study of Structural as well as optical properties of CdSe thin film samples were carried out with respect to annealing temperature [8].

3.0 Results and discussion

The reaction progress of synthesis of CdSe sample can be illustrated as follows.

$CdCO_3 + 2Cl_2CHCOOH \rightarrow Cd(Cl_2CHCOO)_2 + CO_2 + H_2O$ (1) $Cd(Cl_2CHCOO)_2 + NH_3 + H_2O \rightarrow Cd(OH)_2$ (2)

$Cd^{2+} + 4NH_3 \rightarrow Cd(NH_3)_4$ (3)

$Na_2SeSO_3 + 2OH^- \rightarrow Se^{2-} + Na_2SO_4$ (4)

$Cd(NH_3)_4 + Se^{2-} \rightarrow CdSe$ (5)

The deposited CdSe thin films were found to be orange red and annealed films were maroon colored. As deposited and an annealed CdSe thin films were used for structural and optical characterization.

The X-ray diffractogram of as deposited sample is shown in the Fig. 1. As deposited film sample shows amorphous nature of CdSe material. Single high intensity reflection peak is observed in the as deposited film sample at 2θ angle 38 ° due to the 111 hkl planes. The remaining CdSe thin film samples were annealed at 400 ° C and 600 ° C. XRD spectrum of an annealed CdSe thin film sample at 400 ° C is shown in the Fig. 2. An annealed film sample of CdSe at 400 ° C shows reflections due to the (111), (220) and (311) planes with cubic crystal structure. These reflections are well coinciding with JCPDS diffraction patterns from the PDF Card [9]. The Data obtained from X-ray diffraction analysis well matches with other investigators literature value. X-ray diffractogram of an annealed film sample of CdSe at 600 ° C is shown in Fig.3. XRD spectrum shows cubic and hexagonal mixed phases of CdSe film material which is matched with JCPDS Data [10]. The lattice parameters for cubic and hexagonal sample of CdSe film sample have been calculated by using following equations respectively.

$$a = \frac{d\sqrt{h^2+k^2+l^2}}{} \quad \text{----------(6)}$$

$$\frac{1}{d^2hkl} = \frac{4}{3}\left[\frac{h^2+hk+k^2}{a^2}\right] + \left[\frac{l^2}{c^2}\right] \quad \text{.....(7)}$$

The lattice parameter of as deposited CdSe film sample was found to be 5.1886 Å. While for annealed film at 400 C was found to be 5.1760 Å. The Crystallographic parameters of annealed CdSe thin films at 400 ° C are shown in Table 1.

The grain size of CdSe film sample was calculated by using Scherrer formula.

$$D = K\lambda/\beta\cos\theta \quad \text{.....(8)}$$

Where, D is crystallite size, K is constant i.e. 0.9, λ is the wavelength of the x-ray used, β (in radians) is the broadening of diffraction line measured at half of its maximum intensity and θ is Bragg's diffraction angle. The grain size was estimated by resolving the highest intensity peak and plotting Lorentzian fit of 111 planes. The grain size of as deposited CdSe thin film was found to be 194 A° and annealed at 400 C found to be 253 A°. As temperature increased from 400 ° C to 600 ° C, film sample shows phase transformation from cubic to hexagonal phase [10]. The lattice parameter of CdSe film sample at 600 ℃ was found to be a= 4.2788 Å and c=7.0048 Å. shown in the Table 1. The grain size of an annealed film sample of CdSe at 600 ° C is found to be in the order of 421 A°. An annealed film sample shows increase in the grain size.

The optical absorbance study of the CdSe films was carried out on UV- vis-NIR double beam spectrophotometer in the visible range with difference of 2 nm wavelength from 400 to 800 nm. The band gap energy (Eg) was calculated by plotting a graph of $(\alpha h \upsilon)^2$ versus hυ [11]. The linear nature of plot indicates the presence of direct band to band type of transitions of CdSe film sample. For determination of the energy band gap 'Eg' extra plotting the straight line to the energy axis and intercept to the x-axis gives the optical band gap energy. The plot of $(\alpha h \upsilon)^2$ versus h υ of as deposited thin film is shown in the Fig.4. The band gap energy of as deposited CdSe thin films is found to be in the order of 2.2 eV. An annealed CdSe thin film sample shows band gap energy 2.2 eV. An annealed film sample shows increase in the band gap energy due to increase in grain size of CdSe sample which is good agreement in the earlier research investigators [12].

The refractive index of CdSe thin film is calculated by using the following relation [13-14].

$$n = 4.16 - 0.85Eg \quad \text{---------- (9)}$$

As deposited sample of CdSe shows 2.71 refractive index while an annealed sample shows 2.29 refractive index. The refractive index of as deposited sample is greater than an annealed CdSe film sample. This attributed to change in the grain size of the CdSe film material [15].

Conclusions

(i) Effect of air annealing on chemically deposited CdSe thin films have been studied.

(ii) In the X-ray analysis, an annealed CdSe film sample shows phase transformation from cubic to hexagonal phase.

(iii) In the optical analysis, an annealed CdSe thin film sample shows change in the band gap energy from 1.7eV to 2.2 eV.

(iv) CdSe film sample shows increase in the grain size from 194 A° to 421 A° due to air annealing.

(V) Refractive index of as deposited CdSe film sample is 2.71 and an annealed CdSe film sample if 2.29.

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References

[1] Lade, S. J.; Uplane, M. D.; Lokhande, C. D.; Mater. Chem. Phys. **2001,** *68* 36-41.

[2] Ozin, G. A.; Adv. Mater. **1992**, *4*, 612 -649.

[3] Athanassopoulou, M.D.; Mergos, J.A.; Palaiologopoulou, M.D.; Argyropoulos, Th.G.; Dervos, C.T.; Thin Solid Films, **2012**, *520* 6515–

[4] Hankare, P.P.; Khomane, A. S.; Chate, P.A.; Rathod, K.C.; Garadkar, K. M.; J. Alloys Compd, **2009**, *469*,478-482.

[5] Hankare, P.P; Jadhav, A. D; Khomane, A. S; Bhuse.V, M; Garadkar, K. M; Mater. Chem. Phys. **2003**, *80(1)*, 102-107.

[6] Yadav, A. A.; Barote, M. A.; Chavan, T.V.; Masumdar, E.U.; J. Alloys Compd, **2011,** *509*, 916–921.

[7] Khomane, A.S.; Mater. Res. Bull.,**2011**, *46*, 1600-1603.

[8] Laatar, F.; Hassen, M.; Smida, A.; Riahi, R.; Bel Haj Mohamed, N.; Ezzaouia, H.; Superlattices and Microstructures, **2015**, *83*, 575-587.

[9] JCPDS Data File No.00-019-0191.

[10] JCPDS Data File No. 00-002-0330.

[11] Kale, R. B.; Lokhande, C. D.; Semicond. Sci. Technol., **2005**, *20*, 1–9.

[12] Hankare P.P.; Delekar S.D.; Asabe M.R.; Chate P.A.; Bhuse.V,M.; Khomane A. S.; Garadkar K.M.; Mater. Chem. Phys., **2006**, *67(12)*,

[13] Akaltun, Y.; Ali Yildirim M.; Ates, A.; Yildirim, M.; Optics Communications, **2011**, *284*, 2307–2311.

[14] Ravindra, N.M.; Ganapathy, P.; Choi, J.; Infrared Phys. Technol., **2007,** *50*, 21-29.

[15] Ezema, F. I.; Osuji, R.U.; Chalcogenide Letters, **2007,** *4(6)*, 69 – 75.

Figure Captions

[1] Fig.1 XRD - spectrum of as deposited CdSe thin films.

[2] Fig.2 XRD - spectrum of CdSe thin films annealed at 400° C.

[3] Fig.3 XRD - spectrum of CdSe thin films annealed at 600° C

[4] Fig.4 Plot of $(\alpha h \upsilon)^2$ versus $h \upsilon$ of CdSe thin films at 400° C.

[5] Fig.5 Plot of $(\alpha h \upsilon)^2$ versus $h \upsilon$ of CdSe thin films at 600° C.

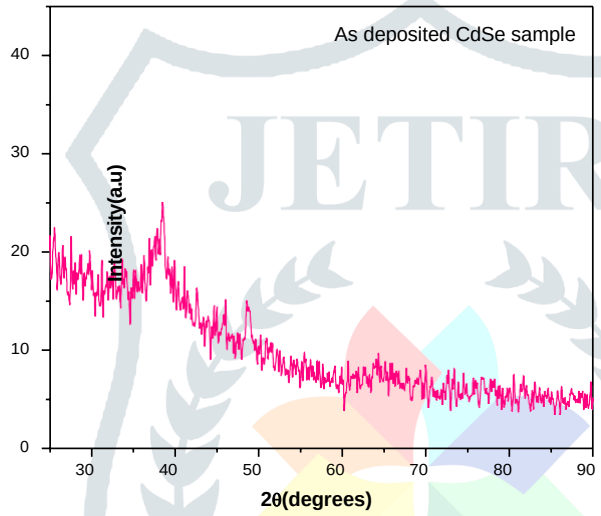

Fig.1

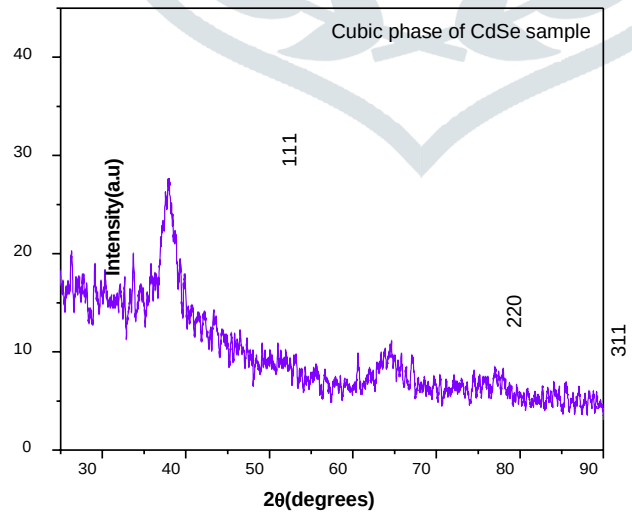

Fig.2

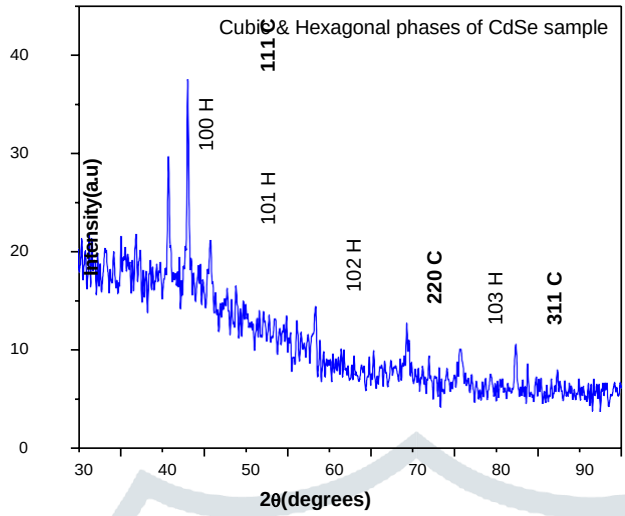

Fig.3

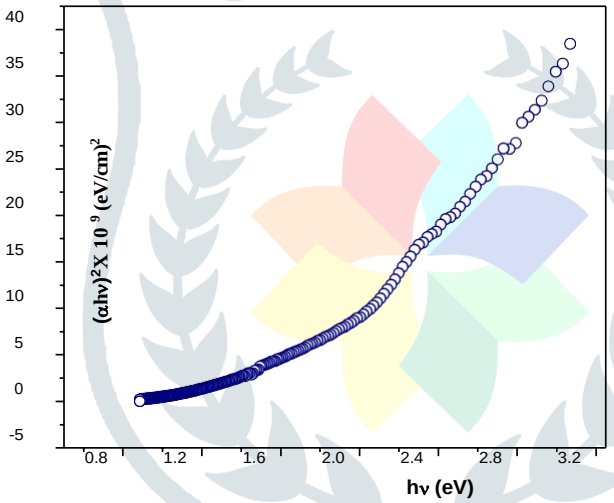

Fig.4

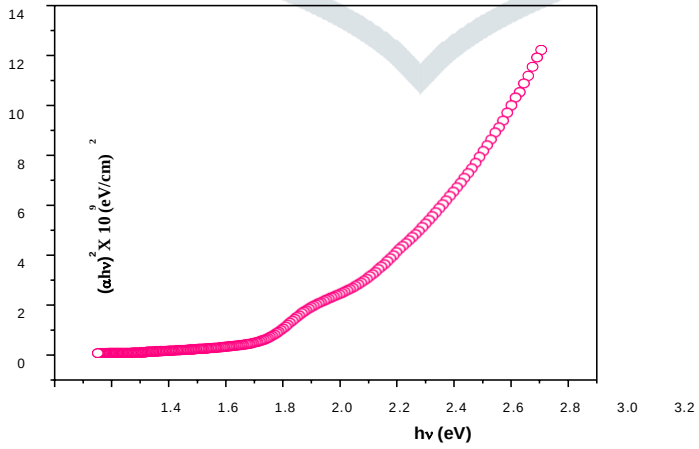

Fig.5

Table Caption

Table.1 Structural parameters of CdSe thin films.

Sample	d-values Å			hkl	Parameter	Grain
	Standard		Observed	planes	cell (A)	size
	Cubic	Hexagonal				
CdSe	3.5100	3.7400	3.5100	111	5.1886	194
As	2.1490	3.5200	2.1489	220		
deposited	1.8330	3.3100	-	311		
		2.1600	-			
		1.9880	-			
		18390	-			
CdSe	3.5100	3.7400	3.4977	111	5.1760	253
An	2.1490	3.5200	2.1462	220		
annealed	1.8330	3.3100	1.8305	311		
at 400 ° C		2.1600	-			
		1.9880	-			
		18390	-			
CdSe	3.5100	3.7400	3.7056	100	a=4.2788	421
An	2.1490	3.5200	3.5024	002	and	
annealed	1.8330	3.3100	3.2641	101	c=7.0048	
at 600 ° C		2.1600	2.1482	110		
		1.9880	1.9579	103		
		18390	1.8294	112		