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Structural, morphological and optical properties of nanocrystalline cadmium selenide thin films

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ABSTRACT

Nanocrystalline cadmium selenide thin films have been deposited on non-conducting glass substrates. The film samples were characterized by XRD, SEM, UV–vis-NIR reflection/absorption spectroscopy and TEP techniques. The annealed film samples showed a crystalline nature with a cubic crystal structure. The optical analysis showed direct band to band type of transition. The band gap of film sample was found to be in the order of 1.7 eV. The electrical conductivity of the film sample was found to be in the order of $10^{-6}\,(\Omega\,\mathrm{cm})^{-1}$. TEP measurements show n-type of conductivity.

1. Introduction

Cadmium selenide (CdSe) is one of the most important semiconducting materials from the II–VI group. CdSe has potential application in the area of electronic and opto-electronics devices as a transistor, sensors, lasers and photo electrode [1–17].

CdSe thin films can be deposited by various techniques such as spray pyrolysis, electro electro-deposition, vacuum evaporation, thermal evaporation, successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) [18–23,10,24–26].

We report synthesis of nanocrystalline CdSe thin films by CBD techniques because it is simple, cheap and suitable for large area deposition of thin films. The deposited film samples were characterized by various techniques such as XRD, SEM and optical absorption/reflection spectroscopy. The electric as well as the thermo-electric properties of films are also studied.

2. Experimental details

2.1. Deposition of CdSe thin films

Nanocrystalline CdSe thin films have been deposited first time by using malic acid as a complexing agent. In the deposition of CdSe thin films cadmium sulphate octahydrate and sodium selenosulphate were used as source of Cd^{2+} and Se^{2-} ions, respectively. The Cd^{2+} ions are complexed with malic acid. The complex slowly releases Cd^{2+} ions from the complex, which are used for the slow and homogeneous deposition of CdSe thin films. For the deposition of film samples, the non-conducting glass plates were used as substrates.

In the deposition of CdSe thin films, 10 ml of 0.25 M Cd^{2+} ions were complexed with malic acid. Ammonia and sodium hydroxide were added in the reaction mixture to maintain the pH of the solution. Then 10 ml 0.25 M sodium selenosulphate was added in above reaction mixture. Then resulting solution was diluted up to 50 ml with distilled water. The pH of the reaction was found to be 7.5. The microglass slides were mounted vertically on a specially designed substrate holder and rotated in the reaction mixture with a speed of 55 ± 2 rpm. As the ionic product of Cd^{2+} and Se^{2-} ions exceeds the solubility product of CdSe, then deposition of CdSe thin films is observed.

The microglass substrates were removed from the reaction mixture after 2.0 h. It is then washed with distilled for several times, dried naturally and kept in a glass desiccator over anhydrous $CaCl_2$. The resultant films were found to be homogenous, well adherent to glass substrate and orange red in color.

2.2. Characterization of film sample

The thickness of the CdSe thin films was measured by weight difference method. Phillips PW-1710 X-ray diffractometer was used for crystallographic analysis of film sample. The film samples were scanned in the range of 20–80° as 2θ using Cu $K\alpha_1$ (wavelength = 2.28970 Å). Cambridge Stereo Scan (USA) scanning electron microscope (SEM) was used for topological analysis of film sample. Before the scanning of film sample, samples were coated with gold–palladium layer by using a polaron SEM sputter unit. 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 electrical conductivity of the film samples was carried out in the temperature range of 300–550 K on Zintek-502 BC Milliohm meter by 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.

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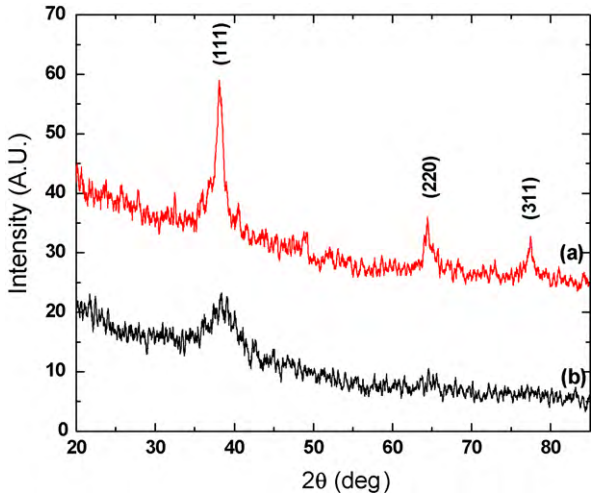

Fig. 1. XRD spectrums of (a) annealed CdSe thin film at 450 °C and (b) as deposited CdSe thin film.

3. Results and discussion

3.1. Growth kinetics

The deposition of CdSe film takes place when the ionic product of Cd^{2+} and Se^{2-} ions exceeds to solubility product of CdSe ($Ks_p = 10^{-33}$). The growth kinetics of CdSe thin films is given below.

$$Cd^{2+} + \rightarrow nMA \rightarrow Cd(MA)_n + 2H^+ \quad (1)$$

where MA = malic acid.

$$Na_2SeSO_3 + 2^-OH \rightarrow Se^{2-} + Na_2SO_4 + H_2O \quad (2)$$

$$Cd(MA)_n + Se^{2-} + 2H^+ \rightarrow CdSe + nMA \quad (3)$$

The color of the deposited CdSe film was found to be orange red. The thickness of the resultant film sample was found to be 0.5 μm.

3.2. Structural analysis

XRD was used for crystallographic analysis of CdSe thin films. X-ray spectrums of annealed CdSe film at 450 °C and as deposited film sample are shown in Fig. 1. A broad hump peak is observed in the 1 1 1 reflection of as deposited film sample due to the presence of amorphous material. 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 investigators report [1–2,16,21–23,28–34]. X-ray diffraction analysis showed that CdSe film sample exhibit in cubic crystal structure.

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

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (4)$$

where '*d*' is the interplanar distance and '*h*, *k*, *l*' are Miller indices of the lattice planes. Crystallographic parameters of CdSe thin films are given in Table 1.

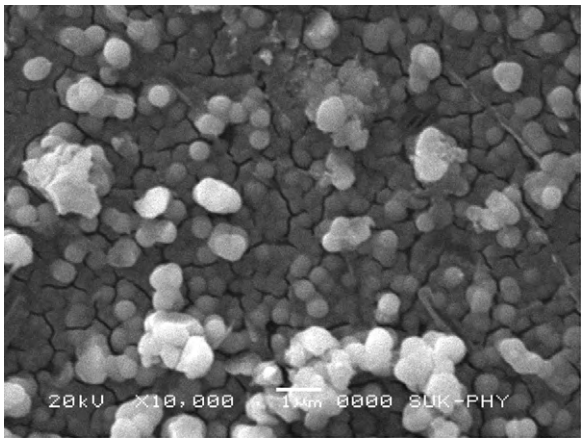

Fig. 2. SEM photograph of annealed CdSe thin film at 450°C.

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

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (5)$$

where *K* is constant (0.94), (is the wavelength of the X-ray used, (is broadening of diffraction line measured at half of its maximum intensity (in rad) and (is Bragg's diffraction angle. The crystallite size of CdSe thin film was found to be 27 nm.

3.3. SEM analysis

SEM was used for surface morphological analysis of film sample. The SEM micrograph of annealed CdSe thin films at 450 °C is shown in Fig. 2. The film samples were uniform, pinhole free and well covered to the glass substrate surface. From the micrograph, it is observed that the film composed of minute grains and uniformly distributed over a smooth homogenous background. The grain size of CdSe film by SEM analysis was found to be 28 nm.

3.4. Optical studies

Optical absorbances/reflections of CdSe films were used for the calculation of band gap energy. It is recorded on UV–vis-NIR double beam spectrophotometer at room temperature. All the absorbances of the film samples were measured in the wavelength range of 400–1400 nm. A careful observation of the spectrum shows the presence of a broad absorption edge in the 600–800 nm range. The absorption data were analyzed using the classical relation for near edge optical absorption of semi-conductors. The relation between the absorption coefficient 'α' and the incident photon energy '$h\nu$' can be given as [35]

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (6)$$

where '*A*' is a constant, 'E_g' is optical band gap of the material and the exponent '*n*' depends upon the type of transition. The values of '*n*' for direct allowed, indirect allowed and direct forbidden transitions are $n = 1/2$, 2, and 3/2, respectively. Optical analysis of film samples

Table 1
Crystallographic parameters of CdSe thin films.

Film sample	*d*-Values (Å)		*h k l* planes	Cell parameter (Å)	Grain size (nm)		Band gap (eV)
	JCPDS	Observed			XRD	SEM	
CdSe	3.5100 2.1490 1.8330	3.5058 2.1489 1.8333	1 1 1 2 2 0 3 1 1	6.0768	27	28	1.7