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X-ray and optical properties of chemically deposited nanocrystalline CdSe thin films

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ABSTRACT

Dip method was used to obtain cadmium selenide (CdSe) thin films on glass substrates. The film thickness was found to be 0.8 μm with a growing time of 5 h. The material obtained was characterized by optical absorption, scanning electron microscopy, X-ray diffraction and electrical measurements. Room temperature deposition results in films with the cubic structure and crystallite size of about 19.7 nm. From the optical absorption data, an energy gap equal to 1.82 eV was found. The material is interesting for applications in hybrid systems for solar energy conversions.

1. Introduction

Thin films of II–VI semiconductors are of considerable interest for their excellent optical properties in the visible range. In particular, cadmium selenide (CdSe) compounds have become quite interesting for solar cells, photodetection and optoelectronic applications [1–2]. It is also used in fabrication of photoelectrochemical cells, non-linear optics, gas sensors, photoconductors, thin film transistors, gamma ray detectors, large screen liquid crystal display, etc. [3–10]. As it is well known that CdSe can be crystallized in zinc blende (cubic), wurtzite (hexagonal) or wurtzite–zinc blende mixed phases, the transformation in crystalline phases of CdSe has attracted much attention in the past [11]. Some researchers observed the phase transformation by annealing [12] or mechanically grinding CdSe samples [13]. Cadmium selenide thin films have been synthesized by using different methods such as electrodeposition [14,15], molecular beam epitaxy [16], spray pyrolysis [17], successive ionic layer of adsorption and reaction [18] and chemical bath deposition [19–22].

In this work, nanocrystalline CdSe thin films were prepared by dip method at room temperature. The X-ray diffraction, scanning electron microscopy, atomic absorption spectroscopy, optical absorption techniques and two-probe technique are used to characterize the CdSe thin films.

2. Experimental details

Cadmium selenide thin films were prepared by dip method on glass substrates. The substrates were cleaned with soap and double distilled water. Sodium selenosulphate was prepared by the following the method, reported earlier [23].

To prepare the bath, 10 mL (0.2 M) cadmium sulphate octahydrate was poured in 100 mL beaker; other chemicals were used in the following sequence: 2.5 mL (1 M) succinic acid, 10 mL (2.8 M) ammonia, 10 mL (0.25 M) sodium selenosulphate. The pH of the reactive mixture is 11.02. The total volume was made 50 mL with double distilled water. The temperature of the bath was maintained at 278 K using ice bath. The solution was stirred vigorously before dipping non-conducting glass substrates. The substrates kept vertically slightly tilted in a reactive bath. The temperature of the bath was then allowed to increases up to 298 K very slowly. After 5 h, the slides were removed washed several times with double distilled water. The film was dried naturally preserved in dark desiccators over anhydrous $CaCl_2$. The film was deposited on both sides of slides.

3. Characterization of cadmium selenide thin films

The thickness of cadmium selenide thin film was measured by weight difference method. Crystallographic studies of cadmium selenide thin film was characterized by using a Phillips PW-1710 X-ray diffractometer with Cu $K\alpha_1$ line ($\lambda = 1.54056$ Å) in 2θ range from 10° to 80°. The optical properties were studied by taking absorption spectra of films using a Hitachi-330 (Japan) double beam spectrophotometer in range from 450 to 750 nm at room temperature. Film microstructure was studied by using 250 MK-III, Stereoscan,

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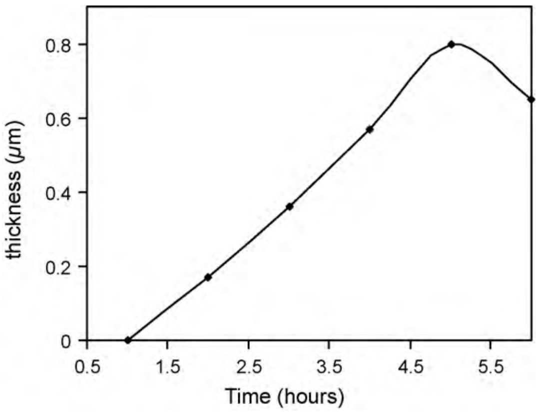

Fig. 1. Variation of the film thickness with deposition time.

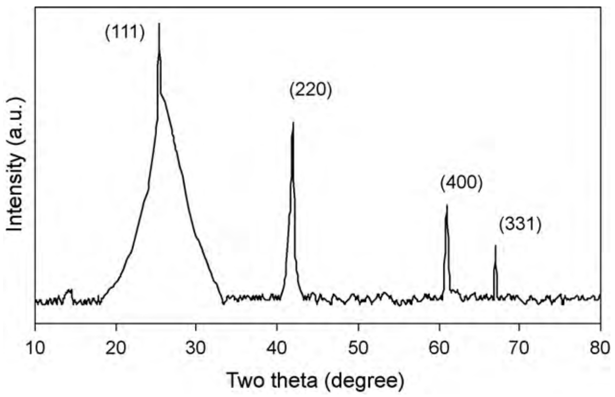

Fig. 2. XRD pattern of cadmium selenide thin film.

Cambridge (UK) scanning electron microscope. The electrical resistance measurements were carried out in the temperature range 300–525 K on a Zintek 502 BC milliohmmeter using two-probe method. Compositional analysis for cadmium was carried out with an atomic absorption spectrophotometer using PerkinElmer 3030, USA.

4. Results and discussions

4.1. Growth mechanism

Cadmium selenide films were deposited by decomposition of sodium selenosulphate in alkaline solution containing cadmium sulphate and succinic acid as complexing agent. Succinic acid controls the cadmium ion concentration in the reaction vessel. As the temperature increases slowly, the decomposition of sodium selenosulphate and metal complex take place in alkaline medium favors the formation of cadmium selenide thin film. The deposition process is based on the slow release of Cd^{2+} ions and Se^{2-} ions in the solution by ion-by-ion basis on the glass substrates. The deposition take place when the ionic product of Cd^{2+} and Se^{2-} greater then solubility product [$K_{sp} = 10^{-33}$]. The growth mechanism of film can be understood from the following reaction:

$$\mathrm{Cd^{2+}} + \mathrm{succinicacid} \rightarrow [\mathrm{Cd\text{-}succinate}] \tag{1.1}$$

$$\mathrm{Na_2SeSO_3} + \mathrm{OH^-} \rightarrow \mathrm{Na_2SO_4} + \mathrm{HSe^-} \tag{1.2}$$

$$\mathrm{HSe^-} + \mathrm{OH^-} \rightarrow \mathrm{H_2O} + \mathrm{Se^{2-}} \tag{1.3}$$

$$[\mathrm{Cd\text{-}succinate}] + \mathrm{Se^{2-}} \rightarrow \mathrm{CdSe} + [\mathrm{succinate}]^{2-} \tag{1.4}$$

Deposition begins only when the chalcogenide concentration is high enough to allow nucleation to start, which occurs in the linear region of growth. As the limiting reactant is used up, growth will start slow down and eventually stop due to depletion of the reactant [24,25]. The behaviour of thickness versus deposition time is showed in Fig. 1. The film thickness increases with immersion time, but after 5 h the growth process reaches the saturation and further only lower thickness value can be achieved. This is mainly due to decrease in concentration of reactant with time as well as dissolution of the film in the solution. The deposited films are orange and transparent. The terminal thickness is found to be 0.8 μm.

4.2. Structural studies

Literature survey revealed that cadmium selenide has two structural phases such as hexagonal wurtzite, cubic zinc blende type [26]. The XRD pattern of cadmium selenide deposited on glass substrate is shown in Fig. 2. The presence of a large number of peaks indicates that the films are polycrystalline in nature. The observed *d* values for sample was in well agreement with the standard *d* value taken from, JCPDS card No. 19-191 and JCPDS card No. 8-459, shown in Table 1, which confirmed that cadmium exists in the sphalerite (zinc blende type) structure. The XRD pattern shows the highest intensity reflection peak at $d = 3.512$ Å (1 1 1). The diffused background is due to amorphous glass substrate and also to some amorphous phase present in the cadmium selenide thin films. Along with (1 1 1) plane, (2 2 0), (4 0 0), (3 3 1) peaks were observed. The lattice parameter of cubic phase was calculated by using standard equation. The lattice parameter '*a*' of film is found to be 6.0768 Å. The-crystallite size of cadmium selenide thin films was calculated by using Scherrer's formula. The average crystallite size was calculated by resolving the highest intensity peak of (1 1 1) plane. The average crystallite size of cadmium selenide thin film was found to be 19.7 nm.

4.3. Microscopic studies

The scanning electron micrograph of cadmium selenide thin film is shown in Fig. 3. It shows that film's surface is covered uniformly. It is clearly seen that the film, composed of minute grains, was uniformly distributed over a smooth homogenous background that may correspond to amorphous phase of cadmium selenide thin film. The presence of fine background is an indication of one-step growth by multiple nucleations.

4.4. Optical studies

The optical absorption spectrum cadmium selenide film onto non-conducting glass substrate was studied at the room tempera-

Table 1
Structural characterization of cadmium selenide thin films.

Film	*d* values		*h k l* planes	Grain size (nm)		Cell parameter (Å)
	Observed	ASTM		XRD	SEM	
CdSe	3.512 2.148 1.518	3.510 2.149 1.519	111 220 400	19.7	20.1	6.0768

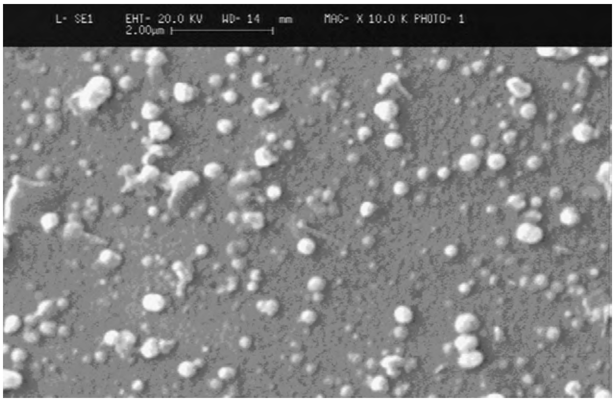

Fig. 3. SEM micrograph of cadmium selenide thin film.

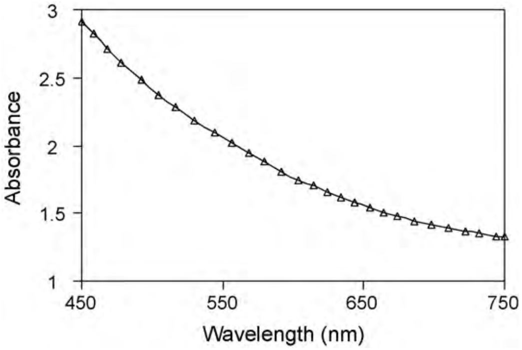

Fig. 4. Absorption spectrum of cadmium selenide thin film.

ture in the wavelength of 450–750 nm. Fig. 4 shows the variation of optical absorbance with wavelength. The optical studies show that the films are absorptive. The data were properly studied in the vicinity of an absorption edge on the basis simplest form of the equation obeyed near and above absorption edge are [27];

$$\alpha = \left(\frac{A}{h\nu}\right)(h\nu - Eg)^n \quad (1.5)$$

where, $h\nu$ is the photon energy, Eg is the band gap, A and n are constants. 'A' is depending upon the temperature, phonon energies, etc. For allowed direct transition $n = 1/2$ and for allowed indirect transition $n = 2$. A plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 5. The linear nature of plot shows that the existence of the direct transitions. Extrapolation of the linear portion of the curve to $\alpha = 0$ gives the optical band gap, which is about 1.82 eV. The value of band gap obtained agrees well with the results of previously reported results [28]. The observed value is greater than standard band gap (1.7 eV) of the cadmium selenide material [29], showing a 'blue shift' of 0.12 eV. The small increase of the band gap in comparison with bulk material could be related with small grain size and/or to stress due to deformation of the film. The plot of ln($h\nu$–Eg) versus ln($\alpha h\nu$) is shown in Fig. 6. The slope of a graph is 0.5, suggests that CdSe show direct type of transitions.

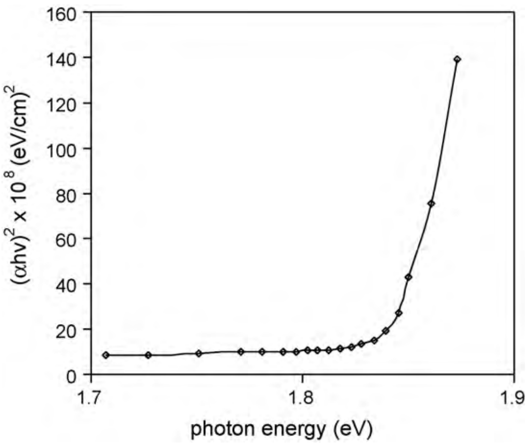

Fig. 5. Plot of $(\alpha h\nu)^2$ with respect to photon energy.

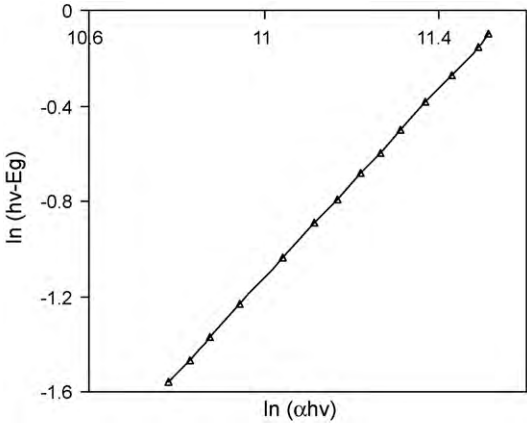

Fig. 6. Plot of ln($\alpha h\nu$) versus ln($h\nu$–Eg).

4.5. Compositional analysis

Atomic absorption spectroscopy was used to study compositional analysis by calibration curve method. Previously weighed minute sample was dissolved in the minimum quantity of conc. HNO_3. Below pH 7, the selenium was precipitated as free metal [30], while nitrates of cadmium remain in the solution state. The precipitated was filtered through a Gooch crucible and subjected to selenium estimation using a standard gravimetric method. The compositional analysis of the sample gave 49.95% cadmium and 50.05% selenium, showing samples is cadmium deficient.

4.6. Electrical conductivity and thermoelectrical studies

The dark electrical conductivity of as grown cadmium selenide film on non-conducting glass slide was determined by using a 'dc' two-probe method, in the temperature range 300–525 K. A plot of log (conductivity) versus inverse absolute temperature for the cooling curve is shown in Fig. 7. It is found that the conductivity during heating and cooling cycles is different and this indicates that the grown films undergo an irreversible transformation due to annealing out of non-equilibrium defects during first heating.

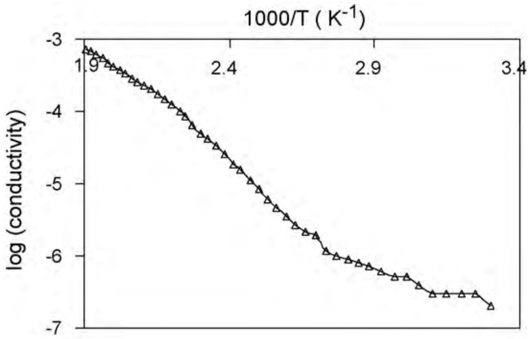

Fig. 7. The variations of log (conductivity) with inverse temperature.

Table 2
Opto-electric properties of cadmium selenide thin films.

Sample	Band gap (eV)	Activation energy (eV)	Specific conductance $(\Omega\,\mathrm{cm})^{-1}$	
			300 K	525 K
CdSe	1.82	0.669	2.01×10^{-7}	7.364×10^{-4}

At room temperature the specific conductance of the film was found to be of order of $10^{-7}(\Omega\,\mathrm{cm})^{-1}$, which is higher than the earlier reported value [31]. The lower value of conductivity may be attributed to grain boundary discontinuities, presence of surface states. Due to grain boundary discontinuities the internuclear space effectively increases and increases the height of the grain boundary potential resulting in a decrease in carrier concentration as well as mobility and hence the electrical resistivity increases. Similarly as shown in compositional analysis the percentage of selenium in the film is higher than percentage of cadmium. The amount of cadmium donar is reduced resulting in increased film resistance. The donor impurities may form shallow levels because of reduction is grain boundary width. The conductivity of film increases with increase in temperature that indicates the semiconducting nature of the film. The dependence is almost linear indicating the presence of only one type of conduction mechanism in the film. The activation energy is calculated using Arrehenius equation. The activation energy obtained from linear portion of a graph is found to be 0.669 eV. The negative terminal was connected to cold end; therefore, the sample exhibits n-type conductivity [32,33].

The various optical and electrical characterization of cadmium selenide thin film such as band gap, activation energy and specific conductance are cited in Table 2.

5. Conclusion

Cadmium selenide thin film can be deposited easily by a low temperature dip type method. The films are orange, polycrystalline in sphalerite cubic structure. The film formation takes place by ion-by-ion growth mechanism. Optical study shows that, the films have high absorption coefficient and band to band transition. Temperature dependence electrical conductivity showed the semiconducting nature of the film. Thermoelectrical power measured shows n-type conduction for cadmium selenide thin film.

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