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Synthesis and Characterization of Cadmium Selenide Thin Films

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Crystalline cadmium selenide thin film has been deposited using appropriate precursor solution containing cadmium sulphate octahydrate, triethanolamine, sodium hydroxide, ammonia solution and sodium selenosulphate. The effect of parameters such as bath composition, deposition temperature, pH of solution, speed of the rotation and the specificity of complexing agent on growth process is studied. The grown films were found to be uniform, well adherent to the glass substrate and specularly reflective. The crystalline phase of the deposited sample was hexagonal wurzite type. The analysis of optical absorption data shows energy band gap energy (E_g) 2.18 eV. The morphological study and compositional analysis of film sample have been discussed. The electrical resistivity of CdSe thin film was found to the order of 10^{-6} (Ω cm^{-1}).

Key Words: Chalcogenides, Thin films, X-Ray diffraction, SEM and EDAX.

INTRODUCTION

Among **II-VI** compound semiconductor, CdSe is an important material for the development of various modern technologies of solid-state devices such as solar cells, high efficiency thin films, transistors, light-emitting diodes, electron beam pumped lasers, electroluminescent devices, γ-ray detectors *etc*.[1-3].

In recent years major attention has been paid to the investigation of electrical and optical properties of CdSe thin films in order to improve the performance of the of the device and also for finding new applications[4-8]. Several methods have been employed for the preparation of thin films of these compounds such as electrodeposition, spray pyrolysis, SILAR method, physical vapour deposition, vaccum deposition, sputtering, *etc*.[9-12]. Chemical deposition of CdSe thin films have been reported by number of investigators[13-15]. Chemical bath deposition is very convenient method for obtaining uniform film under different deposition parameters. In view of this an effort has been made to study the chemical, structural, optical and electrical properties of CdSe thin films by chemical bath deposition method.

EXPERIMENTAL

The chemicals used, such as cadmium sulphate octahydrate, liquor ammonia, selenium metal powder, triethanolamine, sodium sulphite were of analytical grade. The glass substrates were cleaned using chromic acid rinsed with alcohol and distilled water.

For deposition of CdSe thin films, cadmium sulphate and sodium selenosulphate were used as the source of cadmium and selenium ions, respectively. Cadmium selenide thin film was deposited using equimolar volumes of cadmium sulphate complexed with triethanolamine and sufficient amount of aqueous ammonia solution was added to obtain pH 11.50. To this sodium selenosulphate solution was added and finally distilled water. The beaker was then transferred to preheated reactive bath and the temperature was controlled to 50 ± 2 ºC. Cleaned and dried glass substrates were vertically mounted on a specially designed substrate holder which rotates with the speed of 70 ± 2 rpm.

After 2 h, the substrates were removed from the reactive bath. The deposited films were washed with double distilled water dried in air and kept in a dark wooden box.

Characterization of CdSe thin films: Thickness of CdSe film was measured with weight difference density method. The chemical composition of deposited film has been confirmed by using atomic absorption spectroscopy by calibration curve method. The structure of film was analyzed using XRD technique, the surface morphology of the films was investigated by means of SEM. The DC electrical resistivity measurement was carried out using two probe method in temperature range 300-550 K. The optical absorption spectrum was recorded in wavelength range from 400-850 nm using UV-NIR double beam spectrophotometer.

RESULTS AND DISCUSSION

Growth mechanism: The deposition of CdSe was made using reactive precursor solution containing sodium

selenosulphate as the source of selenide ions and cadmium triethanolammine complex as the source of cadmium ions in alkaline medium. In this growth process, triethanolamine (TEA) acts as a complexing agent. The steps involved in the growth mechanism are as follows.

$$Cd^{2+} + n(TEA) \rightarrow [Cd(TEA)_n]^{2+} \quad (1)$$

$$Na_2SeSO_3 + OH^- \rightarrow Na_2SO_4 + HSe^- \quad (2)$$

$$HSe^- + OH^- \rightarrow Se^{2-} + H_2O \quad (3)$$

$$[Cd(TEA)_n]^{2+} + Se^{2-} \rightarrow CdSe + n(TEA) \quad (4)$$

The deposition of cadmium selenide occurs when the ionic product of Cd^{2+} and Se^{2-} exceeds the solubility product. In growth process, no film formation occurs within first 0.5 h. This is the induction period required to form nucleation centers on the substrate. The presence of induction period suggests the ion-by-ion growth mechanism instead of cluster-by-cluster. The duration of film deposition on the glass substrate was studied. In the present investigation, cadmium selenide films have been deposited after 2 min. The film thickness was measured after every 0.5 h and plotted against time as shown in Fig. 1. Increase in deposition temperature favours film formation. The film thickness was measured after every 5 ºC and plotted against temperature as shown in Fig. 2. Good quality, well adherent CdSe films were formed at temperature 323 K. The deposited films are dark orange coloured and transparent. The films are uniform well adherent and reflecting. The terminal thickness is found to be 5500 Å. The best conditions in the deposition process for yielding good quality film were 323 K and 2 h.

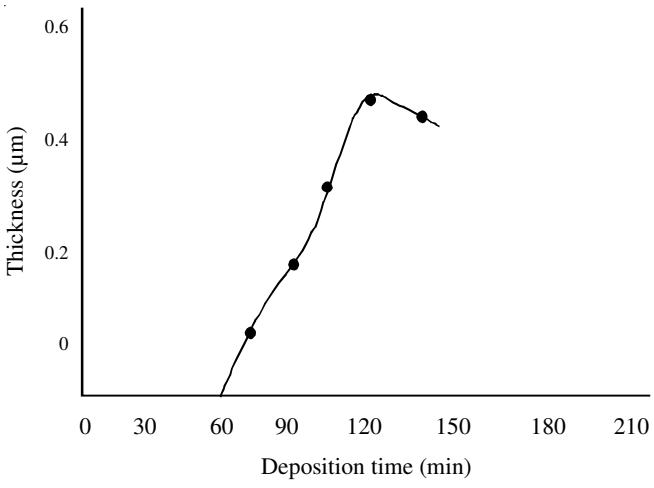

Fig. 1. Variation of the film thickness with deposition time

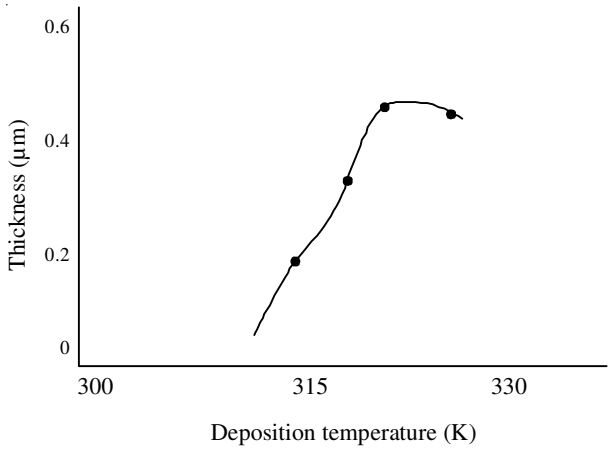

Fig. 2. Variation of film thickness with deposition temperature

Structural studies: The X-ray diffractogram of CdSe obtained has been shown in Fig. 3. From the figure it is evident that there is one peak having very high intensity which appears around angle 25 ºC. The peaks observed have been used to calculate d-spacing and to find the hkl values, cell parameters, crystallite size. These results have been summarized in Table-1. The observed d values corresponds to hexagonal phase of CdSe and therefore are indexed according to hexagonal structure. The lattice parameters for hexagonal phase were determined by using relation.

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{a^2} + \left(\frac{1}{a}\right)^2 \text{ (hexagonal phase)} \quad (5)$$

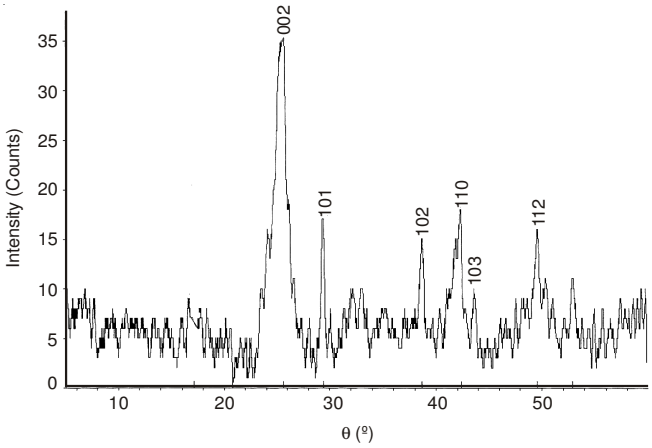

Fig. 3. X-Ray diffractogram for CdSe thin film

The average grain size of the film was evaluated by using Scherrer formula:

TABLE-1
VARIOUS PARAMETERS OF CdSe THIN FILM

d values (Å)		hkl	Grain size (Å)		Activation energy (eV)		Band gap (eV)
ASTM	Observed		XRD	SEM			
3.5050	3.5104	002	3130	3060	0.728	0.288	1.87
3.2880	3.2901	101					
2.5520	2.5486	102					
2.1495	2.1492	110					
1.9800	1.9752	103					
1.8323	1.8246	112					

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (6)$$

The average grain size of the CdSe thin film was found to be 313 Å.

The SEM micrographs of CdSe are as shown in Fig. 4. The film shows smooth and uniform surface with spherical grains of almost similar size. Most of the grains are interconnected to each other and no pores are visible.

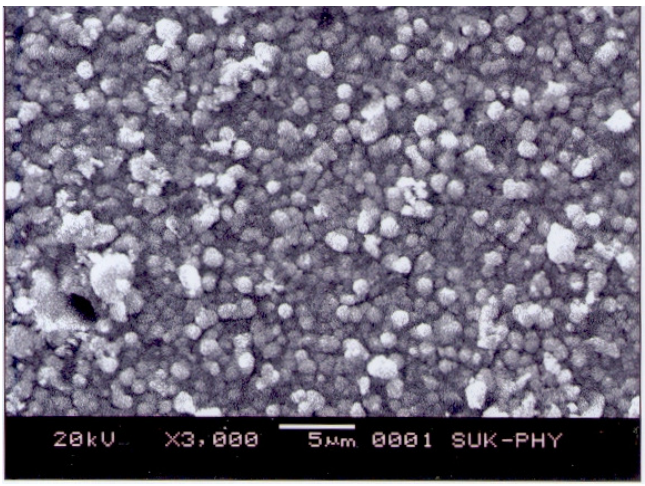

Fig. 4. SEM micrograph for CdSe thin film

Optical studies: The optical absorption of the films has been studied in the range 350-850 nm. The variation of optical density with wavelength is analyzed to find out the nature of transition involved and the optical band gap. Fig. 5a showed that the absorption edge for the sample shifts towards lower energy than that of the as grown samples. This is probably due to increase in the grain size, leading to reduction in the density of grain boundary centers. This shift indicates a decrease in band gap of the sample. The molar absorption coefficient (α) and hence band gap E_g were analyzed at various wavelengths using the following classical relation for near absorption edge in a semiconductor.

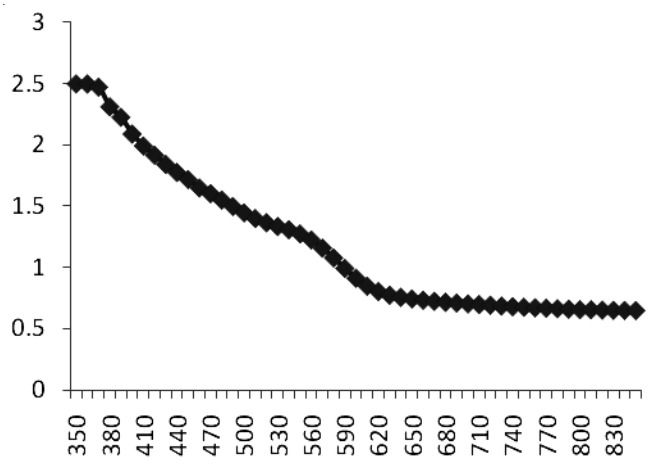

Fig. 5. (a) Variation of α *versus* hν

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (7)$$

A typical plot of $(\alpha h\nu)^2$ with photon energy (hν) for CdSe thin film is shown in Fig. 5b. Extrapolation of the linear portion of the curve gives the optical band gap. The film has band gap 2.18 eV.

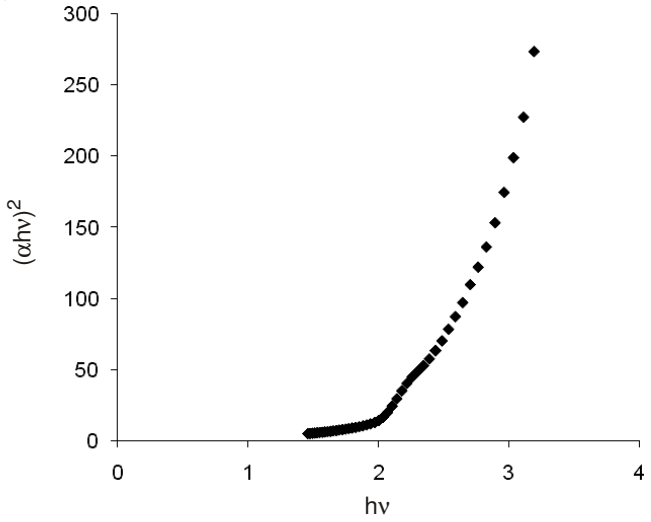

Fig. 5. (a) Variation of log σ *versus* 1000/T

Electrical studies: The electrical resistance of the material was measured by two probe method in temperature range 300-550 K. It is observed that the resistivity decreases with increasing temperature, indicating semiconducting nature. It is well known that electrical properties of polycrystalline thin films are strongly influenced by their structural characteristics[16,17]. The plot of log σ *verses* inverse temperature for this film is shown in Fig. 6. The nonlinear nature of the plot indicates the presence of two different types of conduction mechanism. The temperature dependence of electrical resistivity can be accounted using Arrhenius equation.

$$\sigma = \sigma_0 \exp^{(-E_a/K_T)} \quad (8)$$

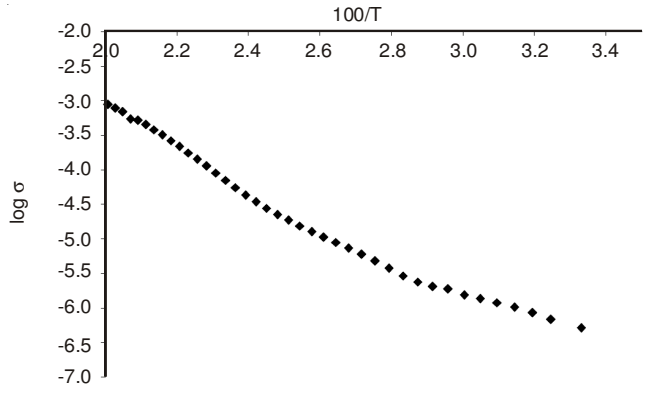

Fig. 6. Variation of log σ *versus* 1000/T

E_a is the activation energy, K is the Boltzmann constant, T is the absolute temperature and σ is the specific conductance. The activation energies obtained from linear portions of graph are found to be 0.288 eV in low temperature region and 0.728 eV in high temperature region.

Compositional studies: The CdSe film was characterized for chemical behaviour using atomic absorption spectroscopy by calibration curve method. Previously weighed minute sample was dissolved in the minimum quantity of conc. HNO_3 to yield the products. The compositional analysis of the sample using AAS gave 50.65 % cadmium and 49.35 % selenium, showing appearance of excess cadmium. The atomic and weight percentage of Cd and Se in CdSe thin film from EDAX are given in Table-2.

TABLE-2
ATOMIC AND WEIGHT PER CENTAGE OF Cd AND Se IN CdSe THIN FILM FROM EDAX

Elements	Observed		Thickness
	Cd	Se	
Wt %	62.53	37.47	5500 Å
At %	53.87	46.13	

Conclusion

CdSe can be deposited easily by CBD. The film growth occur *via* ion-by-ion nucleation method. X-Ray diffractogram shows one peak having very high intensity around 250 which is the dominant peak of (002) plane of CdSe. Film shows polycrystalline hexagonal structure with almost spherical shaped grains. CdSe film shows semiconducting nature. The electrical resistivity is found to be in order 10^{-6} (Ω cm^{-1}). Optical absorption data gives energy band gap for CdSe, 2.18 eV. AAS showing appearance of excess cadmium.

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