

THIN FILMS

## Study of synthesis of nanocrystalline CdS thin film in PVA matrix by chemical bath deposition

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*SUMMARY. – Nanocrystalline thin films of CdS are deposited on glass substrate by chemical bath deposited technique using polyvinyl alcohol (PVA) matrix solution. Crystallite size of the nanocrystalline films are determining from broadening of X-ray diffraction lines and are found to vary from 0.33-0.52 nm, an increase of molarity the grain size decreases which turns increases the band gap. The band gap of nanocrystalline material is determined from the UV spectrograph. The absorption edge and absorption coefficient increases when the molarity increases and shifted towards the lower wavelength.*

### 1. Introduction

The study of nanocrystals one of the most popular field in the scientific community today. The use of thin film semiconductors has attracted much interest in basic research; solid state technology; an expanding variety of application in various electronic and photo electronic devices due to their low production costs.

Cadmium Sulphide (CdS) is one of the promising II-VI compound materials (1-3). In recent years nanocrystalline thin films different II-VI compound semiconductors have been widely synthesized and studied nanocrystalline thin films are also polycrystalline in nature but with sized grains of crystallites of the order of few nanometers (4).

Out of several methods for deposition of nanocrystalline thin film, chemical bath deposition technique in polymer matrix is relatively simple (5). Chemical bath deposition (CBD) can proceed through several different mechanisms which have a role in determining the film properties. The two main basic mechanisms are what commonly termed the cluster mechanism and the ion-by-ion mechanism (6,7). The aim of this work to study the effect of molarities on the structure and optical properties of CdS thin films which prepared by CBD technique.

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## 2. Experimental

Nanocrystalline thin films were deposited on glass substrates by (CBD) technique. Before the deposition of cadmium sulphide on glass slides, the slides (substrate) were cleaned carefully in detergent/cold water, and then rinsed with distilled water and allowed to drip dry in air.

The chemicals that are involved in the growth of cadmium sulphide thin film are:

- a) Cadmium chloride ( $\text{CdCl}_2$ ).
- b) Polyvinyl alcohol (PVA).
- c) Ammonia ( $\text{NH}_4\text{OH}$ ) as a complexing agent.
- d) Thiourea ( $\text{CSNH}_2$ ).

The deposition was carried a mixture of matrix solution and thiourea. The matrix solution was prepared by adding cadmium chloride to an aqueous solution 2% of PVA with constant stirring at a constant temperature  $70^\circ\text{C}$  maintained for 90 mi. Two different concentrations of cadmium chloride (0.1 M and 0.2 M) were used to get different matrix solutions. The solution was the left for 24h to get a transparent liquid indicating completed dissolution of cadmium chloride. The pH of the solution was maintained at around 11 by slowly adding  $\text{NH}_4\text{OH}$  solution, then the equimolar solution of thiourea was added to the mixture solutions and glass substrate were introduced vertically into the solution with the help of a substrate holder with in a few minutes colour of the solution changed to yellow. The substrates were kept in the solution for 3-4 hours at room temperature for deposition of film. After deposition the substrates were taken out and thoroughly washed and rinsed with doubly distilled water and dried in air. Grain sizes of the films were then measured by X-ray diffraction (XRD-6000-Shemadzu) at room temperature with  $\text{CuK}\alpha$  radiation of wavelength  $1.54 \text{ \AA}$  and voltage 40 KV, current 30 mA. Optical absorption spectra at 300K were obtained using Shemadzu UV-160/UV-Visible recorder spectrophotometer in wavelength range 0.2-1.1  $\mu\text{m}$ .

## 3. Result and Discussion

All the measurements were done at room temperature for the films with different molarity deposited by chemical rout. The thickness of the films were 0.0871-0.0452  $\mu\text{m}$ , were measured by the weighting methods. The obtained films were optically transparent, adherent homogeneous and yellow-orange in color.

### 3.1 – XRD studies

The X-Ray diffractogram of CdS show broadened diffraction profiles Fig. 1. It is observed that XRD patterns show a preferred orientation along (100) plane

of the hexagonal phases of CdS film.

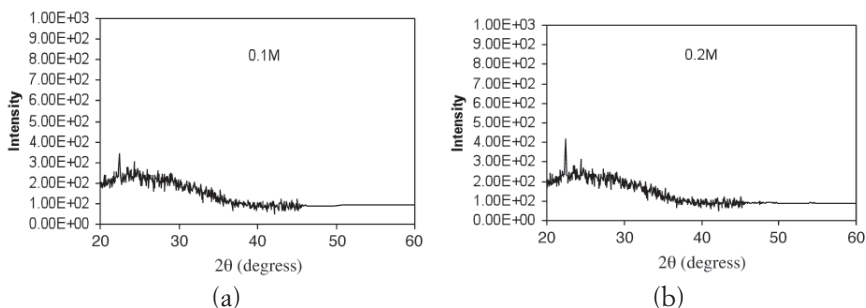


FIG. 1

XRD patterns of CdS nanocrystalline films for two different molarities (0.1M and 0.2M).

The grain size is calculated by the equation

$$[1] \quad D = \frac{k}{\beta_{2\theta} \cos \theta}$$

where  $k = 2\pi/\lambda$  is a constant taken to be 0.94,  $\lambda$  the wavelength of X-ray used ( $\lambda = 1.54 \text{ \AA}$ ) and  $\beta_{2\theta}$  the full width at half maximum of (100) peak of XRD pattern, Bragg angle  $2\theta$  is around 24.4 deg. The values of crystallite sizes of the films were found to be within the range 0.52-0.33 nm. It is observed that crystallite size decreases with increase in molarity (10). The values of crystallite size of the films are shown in Table 1.

Table 1

Molarity	Grain size (nm) from XRD	Energy gap from UV
0.1M	0.52	2.45
0.2M	0.33	2.6

### 3.2 – Absorption studies

The UV absorption of CdS/PVA thin films for different molarities taken at room temperature is shown in Fig. 2. From the spectrograph the absorption edge of the samples are found to occur in the range 300-450 nm, for nanocrystalline films and we can see from the spectrograph the values of absorption increase as the molarity increase and this is due to increase the number of molecules as increase the molarity, and the spectrum shows a clear shift to the lower wavelength side over bulk crystallites which appear clearly in Fig. 3 of the transmission.

This blue shift of the absorption edge indicates decrease of the crystallite size of the sample. CdS is a typical direct band gap semiconductor. According to

Tauc relation the absorption coefficient for direct band material is given by (Tauc, 1974) (8, 9)

$$[2] \quad \alpha = \frac{c}{h\nu} \sqrt{h\nu - E_g}$$

where  $\alpha$  is the absorption coefficient;  $c$  a constant,  $h\nu$  the photon energy and  $E_g$  the band gap. The spectrographs were studied using the standard relation (2). A graph of  $h\nu$  plotted vs  $(\alpha h\nu)^2$  is shown in Fig. 4.

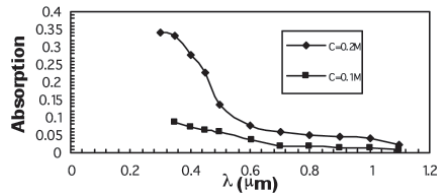


FIG. 2

UV-absorption spectra of CdS nanocrystalline films for different molarities (0.1M and 0.2M).

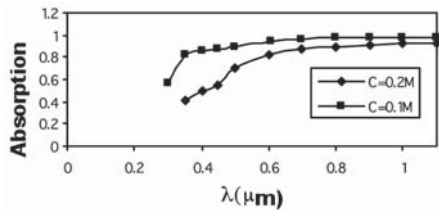


FIG. 3

UV-transmission spectra of CdS nanocrystalline films for different molarities (0.1M and 0.2M).

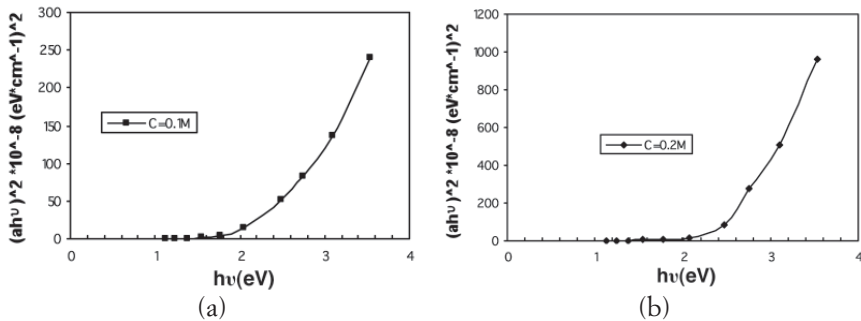


FIG. 4

Energy band gap determination of CdS films for different molarities (0.1M and 0.2M) plotted vs.  $(\alpha h\nu)^2$

The extrapolation of straight line to  $(\alpha h\nu)^2 = 0$  axis gives the value of energy band gap of film materials. The band gap of the films is determined from the plots, and are found to be within 2.45-2.6 eV. The band gap increases with the decrease of crystallite size. This observation of increment in band gap is approximately inversely proportional to the square of the crystallite size based on the effective mass approximation (10).

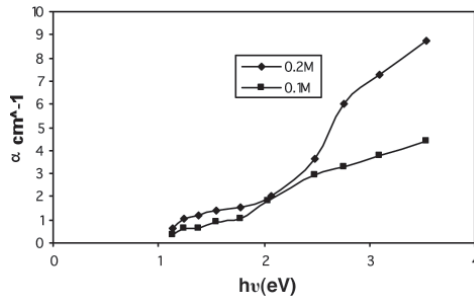


FIG. 5

Absorption coefficient  $\alpha$  as a function of photon energy  $h\nu$  with different molarities (0.1M and 0.2M).

Figure 5 illustrates the relation between absorption coefficient  $\alpha$  and  $h\nu$  for these films.

This figure indicates that the absorption coefficient increases as the molarities increase, so this result agrees with those of E.I. Ugwu and D. U. Onah [11]. Fig. 6 indicates the relation between the refractive index and the wavelength. And we can see from the spectrograph that the refractive index increases as the molarity decrease and the spectrum shows a clear shift to the lower wavelength with increase the molarities (11).

At the last we study the real part of dielectric constant and the imaginary part of the dielectric constant as functions of photon energy, as illustrated in Figs.7 and 8 respectively

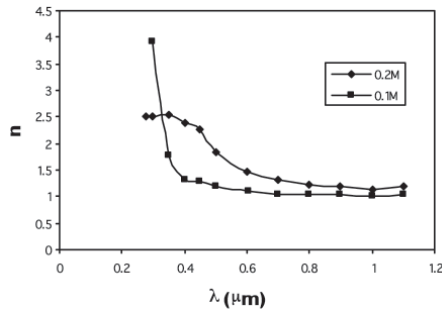


FIG. 6

Refractive index as a function of the wavelength with different molarities (0.1M and 0.2M).

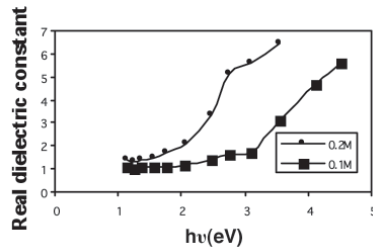


FIG. 7

Real dielectric constant as a function of photon energy with different molarities (0.1M and 0.2M).

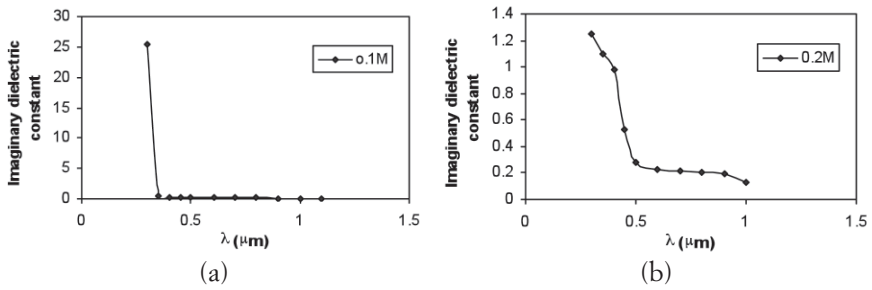


FIG. 8

Imaginary dielectric constant as a function of wavelength with different molarities a) 0.1M, b) 0.2M

We can see from the above figures that the film which has large grain size has high refractive index, lower real dielectric constant, higher imaginary dielectric constant and vice versa (11).

#### 4. Conclusions

Thin films of CdS prepared by CBD technique in PVA matrix are found to be nanocrystalline. The crystallite sizes measured by XRD studies are found to be within 0.33-0.52 nm. The UV absorption studies on films clearly show an increase in band gap which supports the formation of nanocrystallites in these films.

Absorption study was also made to determine the band gap, which also reveals similar fact of an increase of band gap with the decrease in crystallite size and the absorption coefficient increase as the molarities increase. The refractive index increases as the molarity decreases and the spectrum shows a clear shift to the lower wavelengths with the increase of the molarities. The film which has large grain size has high refractive index, lower real dielectric constant, higher imaginary dielectric constant and vice versa. The overall deposition technique

clearly shows that higher molarity facilitates the growth of nanocrystallite in CdS films with PVA matrix.

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