Effect of substrates temperature on structural and optical properties of thermally evaporated CdS nanocrystalline thin films

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Nanocrystalline thin films of CdS were deposited by thermal evaporation technique under vacuum ($p = 2 \times 10^{-5}$ torr) on cleaned glass substrates maintained at different temperatures (300, 473 and 573 K). The effect of substrates temperature on structural and optical properties of CdS nanocrystalline thin films has been studied. X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) and Scanning Electron Microscopy (SEM) were used to characterize the CdS nanocrystalline thin films. The optical and structural studies show that film deposited at 300 K was amorphous in nature and films deposited at higher temperatures were crystalline in nature. Optical constants, such as optical band gap was evaluated from these spectra. The optical band gap was found to be in the range 2.38-~2.51 eV.The study of structural and some physical properties of CdS films indicates that they are strongly dependent on the substrate temperature. Crystallinity levels became better at high substrate temperatures (especially for the film obtained at 573 K). Using the optical investigations including the band gap calculations, it was determined that the band gap of CdS films decreases with substrate temperature, due to the changes in grain size and crystallinity. There is a random effect of substrate temperature on band tail values.

Keywords: Nanocrystalline, CdS, Band gap, Optical properties, Thermal evaporation, Scanning electron microscopy, X-Ray diffraction

1 Introduction

The synthesis and characterization of nanostructure materials have attracted great attention not only because of their exceptional properties[1,2], but also due to their structure and temperature dependent properties and great potential for many practical applications[3,4]. Recently, there has been an increase in research and development of different materials used in devices such as interference filters, optical fibers, optical instruments, coated glazing for windows and solar energy collectors and low cost flat panel solar cells. Thin film devices using optical constant as input data in designing process to give the designer as an additional tool for optimization of the product design, and thus an accurate knowledge of optical constant over wide range of wavelength is essentially important[5,6]. These films offer a larger number of applications in solid-state device technologies such as the target material for television cameras, microwave device, switching devices, infrared detectors, diodes and Hall effect devices.

The various structural and physical properties of CdS thin films prepared by thermal evaporation in different deposition conditions have been discussed in research papers[7-10]. Different techniques have been reported for the deposition of CdS thin films. These including evaporation[11], sputtering[12], chemical bath deposition[13], spray pyrolysis[14], metal organic chemical vapour deposition[15] (MOCVD), molecular beam epitaxial technique[16], electro deposition[17], photochemical deposition[18] etc. In the present work, thermal evaporation technique has been chosen for deposition of CdS thin films because it is trouble-free and controllable technique. In the present work, emphasis has been given on the influence of substrates temperature on structural and optical properties of thermally evaporated nanocrystalline CdS thin films. X-ray diffraction (XRD), ultraviolet-visible (UV-Vis) and Scanning Electron Microscope (SEM) were used to study the structural, optical and surface morphological properties. The nanocrystalline CdS thin films. optical constants, such as optical band

gap, refractive index, and grain size have been evaluated from these spectral studies.

2 Experimental Details

CdS was purchased from Alfa Aesar a Johnson Mathey company with 99.99% purity. CdS nanocrystalline thin films were prepared by thermal evaporation technique at different substrates temperature (300, 473 and 573 K) in a vacuum of 2×10^{-5} torr. Molybdenum boat was used as the evaporation source and glasses were used as substrates which were placed directly above the source at a distance of nearly about 18 cm. The glass substrates were cleaned with freshly prepared acetone, detergent solution and distilled water. Deposition rate and film thickness were controlled by using quartz crystal monitor. The optical transmission spectra for the as-deposited CdS thin films at different substrate temperatures were obtained in the ultraviolet (UV)/visible/near infrared region up to 1100 nm using JASCO UV-Vis spectrometers (Model-Lambda).The structure of the films was studied by using Philips analytical diffractometer type PW3710. Surface morphology of the films were characterized by scanning electron microscopy (SEM; JSM-6380).

3 Results and Discussion

3.1 X-ray diffraction analysis

Figure 1 shows the X-ray diffraction pattern of the CdS thin films deposited at different substrate temperatures. Deposited films were observed to be
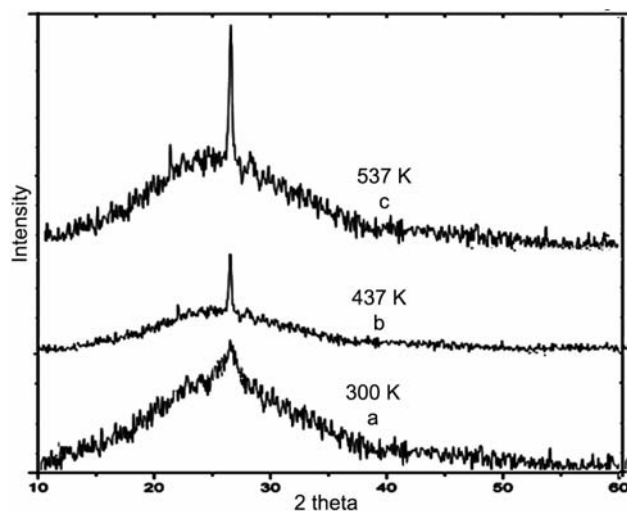

Fig. 1 — XRD spectra of CdS thin films deposited at (a) 300 K, (b) 473 K. and (c) 573 K

uniform, strongly adherent to substrate and orange in colour. The structural property has been observed from the XRD patterns of the CdS thin films deposited at different substrate temperatures 300, 473 and 573 K, respectively. The film shows poor crystalline structure at 300 K as compared to the other films deposited at 473 and 573 K. All the films have a hexagonal structure with a preferred orientation of (002). It has been observed from X-ray diffraction pattern on increasing substrates temperature the crystallinity of thin films gets improved. With the increase of substrate temperature, intensity of hexagonal peak of thin films is also increased.

It has been observed that the FWHM of XRD peak decreases with the increase of temperature. It is well known that the lattice parameters are temperature-dependent, and an increase in temperature leads to expansion of the lattice[19,20]. It is observed that the particle size and lattice parameter of CdS increase with increasing temperature as mentioned in Table 1. It was found that the size of CdS nanoparticles was around 55.0 nm at 300 K, which increased to 78.50 nm when the sample was heated to 573°C.

Further, the crystallites size of the films is estimated using the Sherrer's formula:

$$D = \frac{k\lambda}{\beta_{2\theta} \cos\theta} \qquad \ldots(1)$$

where k is a constant taken to be 0.94, λ the wavelength of X-Ray used ($\lambda=1.54$) and $\beta_{2\theta}$ the full width at half maximum of (002) peak of X-RD pattern, Bragg angle, 2θ, is around 26.420°. The values of crystallites sizes were found to be 55, 63 and 78.50 nm for CdS film prepared at 300, 473 and 573 K, respectively.

The lattice parameters, a and c of the unit cell of the hexagonal CdS thin films were evaluated[10] from Eq. (2):

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \qquad \ldots(2)$$

where d is the interplanar spacing. The calculated lattice parameter values are given in Table 1. According to Ostwald ripening, the increase in the

Table 1 — Lattice parameters at various temperatures

Temperature K	a (Å)	c (Å)
300	----	----
473	4.132	6.741
573	4.141	6.786

particle size is due to the merging of the smaller particles into larger ones and is a result of potential energy difference between small and large particles and can occur through solid-state diffusion[21,22].

3.2 SEM analysis

The scanning electron microscopy (SEM) pictures of the films deposited at different substrate temperatures of 300, 473 and 573 K are shown in Fig. 2(a-c). The SEM micrograph corresponding of CdS thin films deposited at 300 K (Fig. 2a) confirms the amorphous structure of those films, which was obtained from XRD pattern. As seen from the SEM micrograph that the films were uniform, pinhole free and uniformly coated over the glass substrate. Also, it can be observed that there is a great difference between the surface morphology of the film deposited at room temperature, 300 K (Fig. 2a), and the films deposited at substrate temperature of 573 K (Fig. 2c).

The SEM micrograph of all three thin film clearly shows the improvement in crystallite size of CdS thin film with increase in substrate temperature. The micrograph is also revealed the increase in crystallite size with temperature up to about 473 K. The increase of grain size for films deposited at higher substrate temperature, may be attributed to the coalesce of the smaller grains into effectively larger grains[23]. The average crystallite size is found to be 78.50 nm at
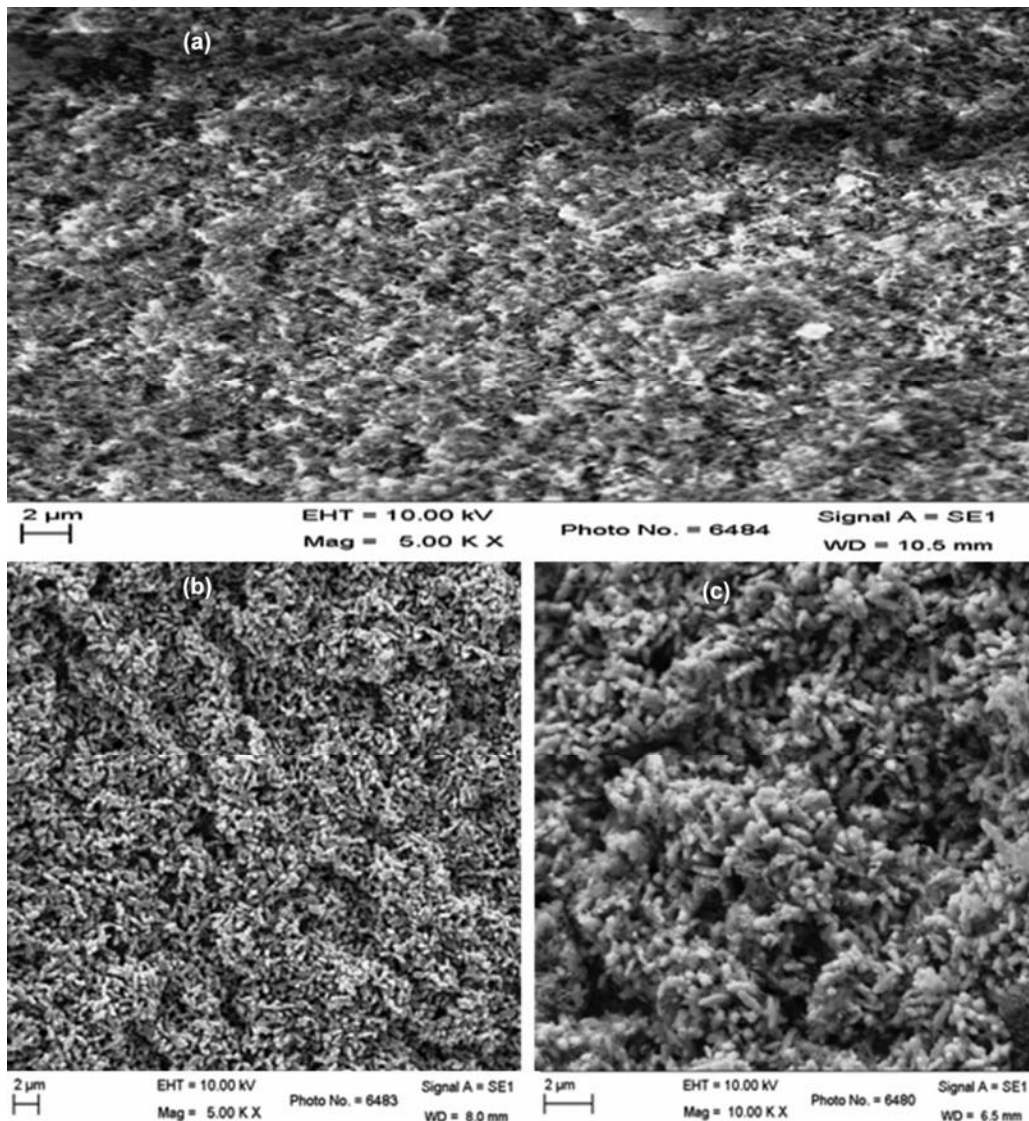

Fig. 2 — SEM micrograph of CdS thin films deposited at (a) 300 K, (b) 473 K. and (c) 573 K

573 K calculated from the XRD pattern. On the other hand, the crystallite sizes revealed from the SEM pictures (74.3-85.9 nm) are higher than the average crystallite size values are from the XRD pattern. Such a difference might be due to the presence of some amorphous phase in the films along with their predominant crystalline phase.

3.3 Optical properties of the CdS thin films

Absorption spectra of the CdS thin films are measured in the UV-visible regions as a function of the substrate temperature. Figure 3 shows typical absorption spectra for the investigation of CdS thin films. It can be observed that the absorption edge shifts continuously to longer wavelength with increase in the substrate temperature. All the films are transparent in the near infrared range of spectra and show good optical transmittance of about 80-85%.

The highest values of the optical transmission are achieved for film deposited at room temperature. Interference maxima and minima due to multiple reflections on the film surfaces can be observed in the transmission spectra. The appearance of interference fringes in these spectra indicates the excellent surface quality and films are free from any inhomogeneity.

The sharp decrease in the optical absorption at the longer wavelength resulted from the excitation of charge carriers across the optical band gap, E_g, which may be estimated by using the following relation and Tauc plot[24]:

$$(\alpha h\nu)^m = A (h\nu - E_g) \qquad \ldots(3)$$

where A is a characteristic parameter independent of photon energy, $h\nu$ the incident photon energy and m is a constant which depends on the nature of the transition between the top of the valence band and bottom of the conduction band. The lowest optical band gap energy in semiconducting materials is referred to as the fundamental absorption edge and nature of interband transition[25] by m. For allowed indirect transition $m=1/2$, and for the allowed direct transition $m=2$, by plotting $(\alpha h\nu)^m$ versus the incident photon energy $(h\nu)$ and extrapolating the straight-line portion of the plots towards low energies, the optical band gap can be obtained as shown in Fig. 4. These plots indicate that the better wider linear regions are observed for the allowed direct transition $(m=2)$ for the CdS nanocrystalline thin films. The values of optical band gap energy for investigated samples are given in Table 2.
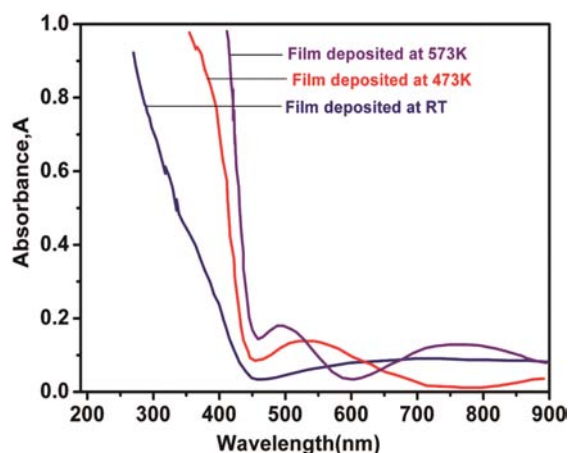

Fig. 3 — Absorption spectra of CDS thin film deposited at different substrate temperature
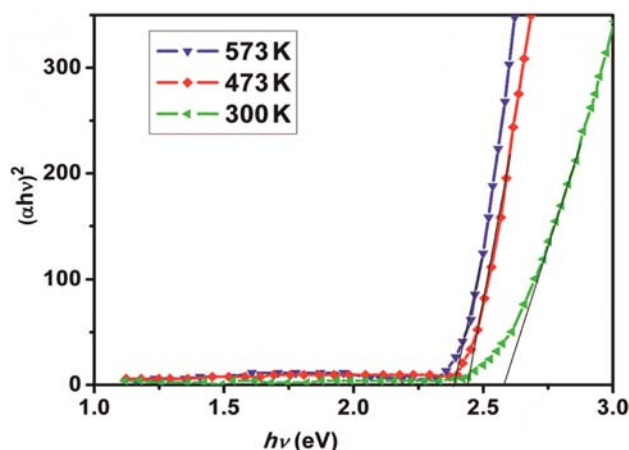

Fig. 4 — Band Gap Plot for CdS thin films deposited at different substrate temperatures

Table 2 — Variation in Band gap with temperature

Samples	T_s (K)	d (nm)	E_g (eV)
1.	300	260	2.51
2.	473	245	2.42
3.	573	283	2.38

From Fig. 4 and Table 2, it can be seen that the optical band gap energy of amorphous CdS thin films was found to gradually decrease from 2.51 to 2.42 eV with the increase of substrate temperature from 300 to 473 K. For CdS thin films deposited at substrate temperature of 573 K, the optical band gap is found to be 2.38 eV. The linear nature of $(\alpha h\nu)^2$ versus $(h\nu)$ plot near the absorption edge confirms that the CdS nanocrystalline thin films are direct band gap material[26]. The estimated values of E_g for investigated

CdS thin films are found to be in good agreement with those published earlier[4,6,8]. The decrease of the optical band gap, E_g, may be attributed the enhancement of grain size, the improvement of the film microstructure and amorphous to nanocrystalline transition occurs by increasing substrate temperature[27,28] to 573 K.

From the band gap values, the particle sizes were estimated using Brus equation[8] :

$$E_{th} = E_g \frac{h^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.786e^2}{\varepsilon R} \qquad \ldots(4)$$

where E_{th} is the band gap of CdS thin films, E_g the band gap of bulk CdS (2.42 eV), m_e^* is the effective mass of electron (=0.19 m_e), m_h^* is the effective mass of the hole (0.8 m_e), ε is the dielectric constant (5.7) and R is the radius of CdS crystallite size. Estimated particle sizes are similar with the experimental results.The investigated films have a specific electron-phonon anharmonocity within pCd-pS structural fragments, which determine their specific temperature changes[29].

4 Conclusions

In the present work, the structural and optical properties of CdS thin films were investigated. Using the thermal evaporation technique, amorphous and polycrystalline thin films of CdS have been prepared. Optical and SEM measurements showed that the structure of the CdS thin films is greatly dependent on the substrate temperature. Thin films deposited at substrate temperature of 300 K are amorphous and those deposited in the range 473-523 K were found to be nanocrystalline with hexagonal crystal structure. SEM micrograph of polycrystalline films shows that the crystallites with average grain size around 74.3-85.9 nm are uniformly distributed over a glass substrate. Also, the optical transition is significantly being affected by the change in structure of the films. The analysis of the optical absorption spectra revealed an allowed direct transition for both type of films amorphous and nanocrystalline. The direct band gap of amorphous films decrease from 2.51 to 2.42 eV as the substrate temperature increases from 300 to 473 K and 2.38 eV at 573 K substrate temperature.

References

1 Mathew X, Enriquez J Pantoja, Romeo A & Tiwari A N, *Sol Energy*, 77 (2004) 831.
2 Sharma R K, Jain K & Rastogi A C, *Curr Appl Phys*, 3 (2003) 199.
3 Ullrich B, Tomm J W, Dushkina N M, Tomm Y, Sakai H & Segawa Y, *Solid State Commun*, 116 (2000) 33.
4 Brit J & Ferekides, *Appl Phys Lett*, 629 (1993) 2851.
5 Tetsuya K, Guan G Q & Akira Y, *Chem Phys Lett*, 371 (2003) 563.
6 Singh A, Sreenivas K, Katiyar R S & Gupta V, *J Appl Phys*, 102 (2007) 074110.
7 Bilgin V, Kose S, Atay F & Akyuz I, *Materials Chem & Phys*, 94 (2005) 103.
8 Elashmawia I S, Hakeem N A & Selim M Soliman, *Materials Chem & Phys*, 115 (2009) 132.
9 Tigau N, *Cryst Res Technol*, 43(9) (2008) 964.
10 Ravichandran K & Philominathan P, *Appl Surface Sci*, 255 (2009) 5736.
11 Senthil K, Mangalraj D & Narayandass S K, *Appl Surf Sci*, 169 (2001) 476.
12 Taneja P, Vasa P & Ayyub P, *Mater Lett*, 54 (2002) 343.
13 Bhushan S & Sharma S K, *J Phys D Appl Phys*, 23 (1990) 909.
14 Baykul M C & Balcioglu A, *Microelectron Eng*, 51 (2000) 703.
15 Tsuji M, Aramoto T, Ohyama H, Hibino T & Omura K, *J Cryst Growth*, 214 (2000) 1142.
16 Yoshihiko S, Takashi O, *J Vac Soc Jpn*, 43 (2000) 284.
17 Nishino J, Chatani S & Y Uotani, Nosaka Y, *J Electroanal Chem*, 473 (1999) 217.
18 Padmavathy R, Rajesh N P, Arulchakkaravarthi A, Gopalakrishnan R, Santhanaraghavan P & Ramasamy P, *Mter Lett*, 53 (2002) 321.
19 Lamber R, Wetjen S & Jaeger N I, *Phys Rev* B, 51 (1995) 10968.
20 Banerjee R, Sperling E A, Thompson G B, Fraser H L, Bose S & Ayyub P, *Appl Phys Lett*, 82 (2003) 4250.
21 Nanda K K, Kruis F E & Fissan H, *Phys Rev Lett*, 89 (2002) 256103.
22 Fang Z B, Gong H X, Liu X Q, Xu D Y, Huang C M & Wang Y Y, *Acta Phys Sin*, 52 (2003) 1748.
23 Kale R B & Lokhande C D, *Mat Res Bull*, 39 (2004) 1829.
24 Tauc J, *Optical properties of Solids*, North-Holland Publishing, Amsterdam, 1972.
25 Kazmerski L L, *Polycrystalline and Amorphous Thin Films and devices*, Academic Press, New York, 1980.
26 Ehsan K & Tomlin S G, *J Phys D Appl Phys*, 8 (1975) 581.
27 Rusu G I, Ciupina V, Popa M E, Prodan G, Rusu G G, & Baban C, *J Non-Cryst Solids*, 352 (2006) 1525.
28 Sridharan M G, Narayandass Sa K, Mangalaraj D & Lee H Chul, *J Optoelectron Adv Mat*, 7 (2005) 1483.
29 Kityk I V, *J Phys Chem B*, 107 (2003) 10087.