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Microstructure, optical and photoluminescence properties of simple thermal evaporated CdS nanocrystalline films

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CdS nanocrystalline films were deposited on glass substrates by thermal evaporation at 300 K and 573K. All the films exhibited wurtzite structure with crystallite size varied from 10 - 20 nm. The sharp sudden fall of optical transmittance spectra shifted from 485 nm to 455 nm with increasing substrate temperature. The excitation wavelength of all films is about 500 nm and emission wavelengths 545 nm and 570 nm for all films. The possible optical and photoluminescence mechanisms are proposed in this paper. The photoluminescence of CdS nanocrystalline films enables them to have important applications in optoelectronic devices.

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Keywords: CdS nanocrystalline films, Resistive thermal evaporation, Microstructure, Optical properties, Photoluminescence properties.

1. Introduction

CdS is an II-VI compound semiconductor and has an energy band gap of 2.42 eV at room temperature in bulk materials. CdS is one of the important materials for application in electro optical devices such as photo conducting cells, photo sensors, transducers, piezoelectric devices, laser materials, display devices, optical wave guides and non-linear integrated optical devices [1 - 5]. In the utilization of the CdS films for electro-optical applications, crystalline quality of the film plays an important role. Substrate temperature leads to improvement in the crystalline quality of the films by the removal of random strain, which can be leads to changes resistivity. The inclusion of this layer is essential for high efficiency solar cells, but its role has been the subject of debate. Earlier workers have been reported both cubic and hexagonal films can be deposited, but for solar cell applications, hexagonal structured films are preparable [6]. Cadmium Sulphide (CdS) is an important material which can be used to make n-type materials for this film hetro-junction solar cell. CdS thin films can be prepared by different techniques such as chemicals bath deposition (CBD) [7, 8] electrodepositon [9] laser ablation [10] sputtering [11] and vacuum evaporation [12]. Among these vacuum evaporation technique is a well established technique. In the present study annealing effect on the morphological, structural and the optical properties of CdS nanocrystalline films were studied and are reported in this paper.

2. Experimental procedure

Cadmium Sulphide films were prepared by thermal evaporation technique on Corning 7059 glass substrates at 300 K and 573 K. The CdS with 5N purity was used as a source material and evaporated from the molybdenum boat. The source to substrate distance was maintained at $\sim$15 cm to get a deposition rate of ~20 A^0/s. Every time, known fixed quantity of material was loaded in the boat and was completely evaporated. The thicknesses of the films were ~0.5 μm. The depositions were carried out in a high vacuum system having diffusion pump backed by rotary pump and with liquid nitrogen trap. Coatings were carried out in the pressure range of 2×10^{-6} m bar. Radiant heater was used to heat the substrate and the thickness of the films was monitored using a quartz crystal thickness monitor (Model QTM101). A temperature controller was employed for controlling the substrate temperature with an accuracy of $\pm$ 2 ^oC.

The deposited CdS films were subjected to various characterization studies. The compositions of the films were estimated using Energy Dispersive Analysis of X-rays (EDAX) attached to Scanning electron microscopy (SEM). The grain size and rms surface roughness of the films were obtained by Atomic Force Microscopy. The structure of the films was studied using powder X-ray diffractometer (XRD) in the scanning range of $2\theta = 10 - 70^0$. Optical properties of the films were investigated by UV/VIS/NIR Spectrophotometer. The photoluminescence properties are studied at room temperature by Fluorolog-3 fluorescence spectrometer.

3. Results and discussions

The thickness of CdS films has been found to be ~0.5 μm. All the films are smooth, pinhole free and strongly adherent to the surface of the substrate. The color of the as-deposited films changed from light yellow to

thick yellow and adherence also increased with the increase of substrate temperature (T_s).

3.1. Composition and structural analysis

Chemical compositions of the constituents in the coatings, obtained from EDAX did not deviate much from the starting material composition. It is within ± 0.02 at. %. The EDAX spectrum of CdS films deposited at 573 K is shown in Fig. 1.

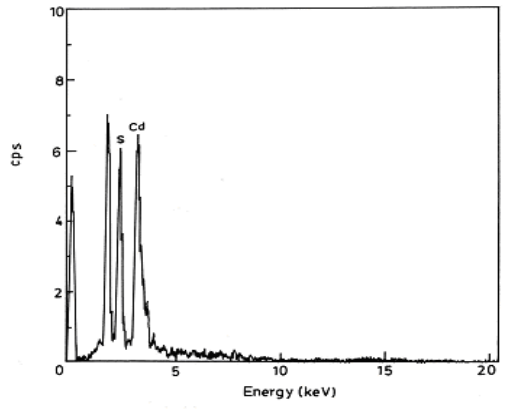


Fig. 1. The EDAX spectrum of CdS films deposited at 573 K.

The XRD spectra of CdS films prepared at 300 K and 573 K are shown in Fig. 2. It can be noted that all the XRD peaks of CdS films are about 26.45^0 - 26.82^0 (2θ), and are similar to the value of 26.4^0 of the (002) orientation of CdS. When viewed with computer software more peaks diffracted nearly at 28.26^0, 48.13^0 and $54,53^0$ respectively corresponding to (101), (103) and (004) planes are observed.

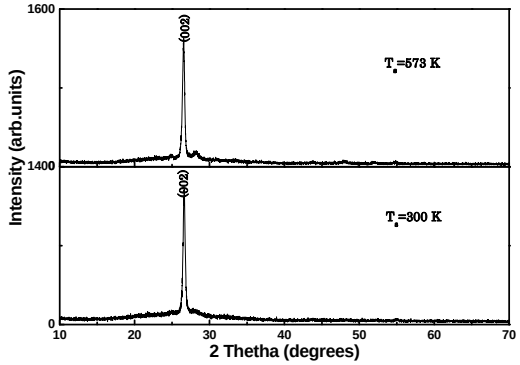
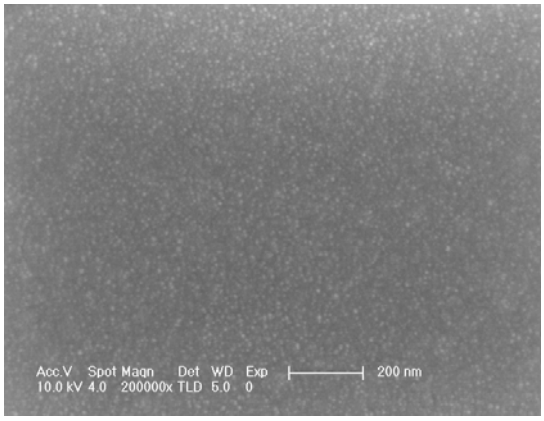


Fig. 2. The XRD spectra of CdS films deposited at 300 K and 573 K.

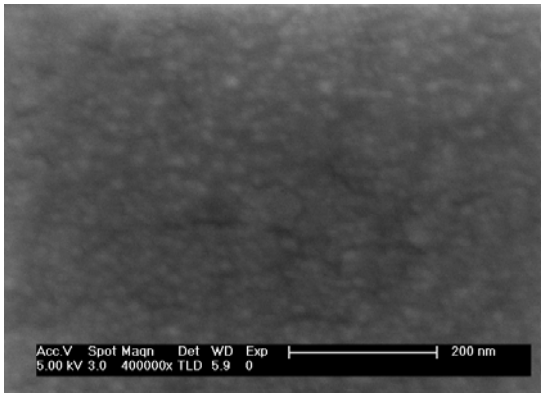
Earlier workers [13, 14] also reported wurtzite structure in nano structured CdS gold nano particles prepared by solution method [13] and by chemical deposition technique [14]. In the present study the average particle size of as-deposited films of all compositions was estimated from XRD peaks using Debye Scherrer formula and was found to lay in the range 10 - 20 nm. In the present work the grain size increased with increasing substrate temperature. Similar variation in particle size was also observed in AFM and SEM studies given in the next section.

3.2. Surface topology and morphology studies

The surface topology of the CdS films carried out by SEM reveals appreciable difference with substrate temperature.



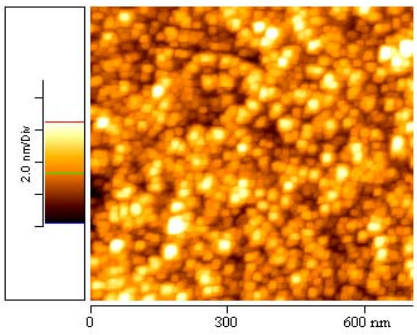
(a)



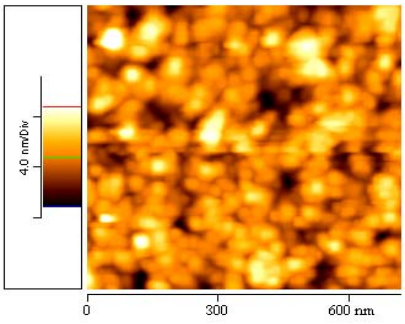
(b)

Fig. 3. SEM images of (a) CdS films deposited at 300 K and (b) deposited at 573 K.

All the as-deposited films have seems to be a small granular structure and high substrate temperature films have big granular structures. The SEM micro graphs are shown in Fig. 3. The surface morphology of all the as-deposited films was studied using AFM. The AFM pictures for are shown in Fig. 4. The images were taken in an area of $0.8 \times 0.8\ \mu m^2$.



(a)



(b)

Fig. 4. AFM images of (a) CdS films deposited at 300 K and (b) deposited at 573K.

The surface morphology of CdS films changes with increasing substrate temperature. The grain size (10 - 20 nm) evaluated from this study is comparable with the data obtained from XRD studies. The surface roughness increased with 'T_s' i.e. the number of voids on the surface of the films decreased with increasing T_s.

3.3. Optical properties

The optical transmittance (T) of the films was studied in the wavelength range 300-1800 nm at room temperature with unpolarised light at normal incidence. Fig. 5 show the optical transmittance as a function of wavelength for the films prepared at 300 K and 573 K.

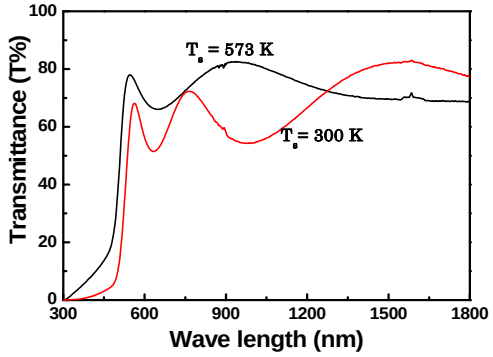


Fig. 5. Variation of transmittance with wavelength for CdS films deposited at 300 K and 573 K.

The optical spectra of the CdS films exhibited interference pattern with a sharp fall in transmittance at the fundamental absorption edge at a wavelength treated as a critical wavelength (λ_c), showing good crystallinity. The absorption edge lies in the range 490 - 460 nm in the present films. The absorption edge shifted from higher wavelength region to lower wavelength region with increase of substrate temperature. The absorption coefficient (α) of the films was obtained from the optical transmittance data and is found to be greater than 10^4 cm^{-1} above the fundamental absorption edge. The variation of absorption coefficient α, with photon energy $h\upsilon$, was linear indicating that the absorption near fundamental edge is direct and allowed. The energy band gap (E_g) has been estimated using the standard equation, $(\alpha E)^2 = E - E_g$, where E is the incident photon energy. The E_g value increased from 2.53 eV- 2.69 eV with increase of substrate temperature. Thus the optical band gap is found to increase with increasing substrate temperature. The extinction coefficient of the CdS films was estimated using the relation,

$$k = \alpha\lambda/4\pi$$

Where 'λ' is the wavelength of incident light. The evaluated extinction coefficient, 'k' decreased with increasing substrate temperature. The evaluated extinction coefficient, 'k' changed from 0.48 to 0.42 with increase of substrate temperature. It can be seen that a sudden fall in 'k' appeared for all films at the critical wavelength (λ_c), above which the increase in 'k' was slow. The refractive index of the CdS films was estimated from the optical data using the standard relation

$$n = [N + (N^2 - n_1^2 n_2^2)^{1/2}]^{1/2}$$

Here

$$N = [(n_1^2+n_2^2)/2 + 2n_1n_2 (T_{max}-T_{min})/T_{max}\, T_{min}]$$

Where n_1 is the refractive index of air, n_2 the refractive index of the substrate, T_{max} and T_{min} are the transmittance maxima and minima at a given wavelength. The refractive index of the films increased with substrate temperature and the value lies in the range 2.23 – 2.43 for all films. Further, it obvious that the refractive index decreased rapidly with wavelength upto the critical wavelength λ_c and above this it varied slowly. The initial sharp decrease of 'n' with 'λ' indicated a rapid change in the absorption energy of the material below 'λ_c'.

3.4. Photoluminescence

The PL spectrum is shown in Fig. 6 of the CdS films prepared at 300K and 573 K. The excitation wavelength for all samples is about 500 nm.

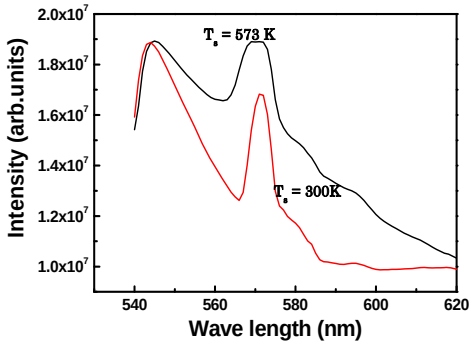


Fig. 6. Variation of PL spectra of CdS films deposited at 300 K and 573 K.

The photoluminescence spectra for all samples consist of two prominent broad bands approximately at 545 nm and 570 nm which are due to recombination of excitons bound to neutral donors. Since the energy separation between the yellow band and the band-to-band transition is approximately 0.16 eV, this probably excludes the possibility of the recombination of free electrons with holes localized at $V_{Cd\text{-}S}$. For high substrate temperature CdS films, the maximum photoluminescence intensity were observed, the intensity decreased together with a broadening of the FWHM (Full width half maximum) of each band.

The PL behavior of the CdS nanostructured materials have been studied intensively [15]. According to previous studies, generally there are two PL emission of CdS nanostructures, namely band edge and surface-defect emissions. Due to the quantum confinement effect, the PL peak positions of the band-edge emission of the nanostructures are strongly size-dependent and usually in the wavelength range of 420-500 nm for CdS [16]. On the other hand, the surface-defect emission is caused by surface states such as sulphur vacancies and/or sulphur dangling bonds. The PL peak positions of the surface-defect emissions are usually in the wavelength range of 530-680 nm [17]. In our case, because of the pretty large grains, the quantum confinement effect can not be used to explain the blue emission at 485 nm (2.56), with about 0.14 eV blue shift compared with the bulk crystal introduced during the preparation process. The green emission at 545 nm and yellow emission at 570 nm are attributable to the recombination of an electron trapped in a sulfur vacancy with a hole in the valence band of CdS [15]. The electrons and holes created by photon absorption can form the excitons which are trapped into the $V_{Cd\text{-}S}$ composite vacancy through a nonradiative process.

4. Conclusions

Simple in-expansive thermal evaporation technique was used to prepare CdS nanocrystalline films on glass substrates at 300 K and 573 K. All the films exhibited wurtzite structure and crystallite size varied from 10-20 nm. SEM micrographs of the samples indicated that the films had small granular structures. AFM studies showed that the films were nanocrystalline in nature. Optical behavior of the films was investigated at room temperature. It has been found that the films showed higher absorption coefficient, $>10^4$ cm^{-1}, and exhibited direct allowed transitions. The optical band gap of the films increased from 2.53 – 2.69 eV with increasing substrate temperature. The photoluminescence behaviour of the films was obtained at room temperature. The peak position is visually not shifted and peak intensity was increased with substrate temperature.

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