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Structural and optical properties of CdS thin film obtained by chemical bath deposition and effect of annealing

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Cadmium sulphide (CdS) thin film was deposited on glass substrate by chemical bath deposition (CBD) by single dip method. The bath-temperature was at 80°C and *p*H at 11. The film was annealed in air at 300°C for one hour. The as-deposited and annealed films were characterized by XRD, UV-visible spectrophotometer, EDAX and photoluminescence study. The film-thickness of 391.1 nm was revealed by Ellipsometry. Coexistence of hexagonal and cubic structure of the as-deposited film was confirmed by XRD. On annealing, the film was confirmed to be purely hexagonal. The band gaps of 2.35 eV of the as-deposited film and 2.29 eV of the annealed film were derived from the optical transmittance data of UV-VIS spectrum. Photoluminescence (PL) spectrum of the CdS thin film exhibits green and red emission peaks with different intensity on annealing. EDAX spectrum confirms the transformation of CdS thin film from off-stoichiometric to near stoichiometric state on annealing.

Keywords: II-VI Semiconductor, Thin film, Chemical bath deposition, Annealing, Structural properties, Optical properties

1 Introduction

CdS thin film is a direct band gap (2.42 eV) metal chalcogenide II-VI semiconductor with high index of refraction (2.5) and *n*-type conductivity[1]. CdS is the best visible light active semiconductor photocatalyst[2]. It is a potential candidate for application as window layer in photovoltaic cell[3], multilayer light emitting diodes[4,5], photo detector, thin film field effect transistor[6], gas sensor and optoelectronic device[7]. CdS thin film can be prepared by vacuum evaporation[8], molecular beam epitaxy[9], sputtering[10], spray pyrolysis[11], electrochemical deposition[12], pulsed laser deposition[13], metal organic chemical vapour deposition[14], successive ionic layer adsorption and reaction[15] and chemical bath deposition[16] (CBD). The most inexpensive method allowing for large area deposition makes CBD an appropriate method for industrial applications. The crystalline quality of CBD-CdS film suitable for electro-optical applications can be achieved by annealing with the removal of random strain in the film. The effect of annealing the CBD-CdS thin film on its structural and optical properties is presented in this paper.

2 Experimental Details

CdS thin film was deposited on a soda lime glass substrate (7.5×2.5×0.145 cm^3). The substrate was cleaned with distilled water, liquinox soap, soaked in dilute hydrochloric acid for one day, washed with ethanol, acetone and finally with distilled water and oven-dried for one hour. The stock-solutions of cadmium sulphate ($CdSO_4$), thiourea [$CS(NH_2)_2$] (Sigma-Aldrich AR grade) were prepared using distilled water. 2.5 ml of 1 M $CdSO_4$ solution was taken in a 250 mL glass beaker. 150 ml of 10 M ammonium hydroxide (NH_4OH) was added till the initially formed white precipitate of cadmium hydroxide $Cd(OH)_2$ in the bulk of the solution dissolved completely. The *p*H was maintained at 11 using NH_4OH. The bath was placed over a heater cum magnetic stirrer (Remi) and temperature was set at 80°C. The cleaned substrate was dipped in the bath-solution with its plane inclined to the surface of the solution. To promote gravity-assisted deposition steadily (laminar flow), 10 ml of 1 M thiourea solution was poured on the substrate through a funnel. The formation of CdS was indicated by slow appearance of yellow colour. After a deposition-time

of one hour, the substrate was removed, cleaned with distilled water and dried in air at room temperature. Adherent, transparent and yellow coloured CdS thin film was obtained (Fig. 1). The CdS thin film was characterized before and after air-annealing at 300°C in a polymer furnace for one hour.

2.1 Mechanism of CdS reaction

NH_4OH reacts with $CdSO_4$ in the aqueous medium resulting in a white precipitate of $Cd(OH)_2$:

$$CdSO_4+2NH_4OH\leftrightarrow Cd(OH)_2+(NH_4)_2SO_4 \quad \ldots(1)$$

On adding excess of NH_4OH, the $Cd(OH)_2$ gets dissolved forming tetra amine cadmium (II) ($[Cd(NH_3)_4]^{2+}$) and hydroxyl ion (OH^-):

$$Cd(OH)_2+4NH_4OH\leftrightarrow[Cd(NH_3)_4]^{2+}+2OH^-+4H_2O \ldots(2)$$

On adding thiourea solution, reaction with OH^- results in the formation of CN_2H_2 and SH^-:

$$CS(NH_2)_2+OH^-\leftrightarrow CN_2H_2+SH^-+H_2O \quad \ldots(3)$$

SH^- combines with $[Cd(NH_3)_4]^{2+}$ to form CdS with the liberation of ammonia gas:

$$[Cd(NH_3)_4]^{2+}+SH^-\leftrightarrow CdS+NH_4^++3NH_3\uparrow \quad \ldots(4)$$

3 Results and Discussion

The film was characterized before and after annealing. The film-thickness was measured using J A Woollam Co., Inc. M2000U ellipsometer. The X-ray diffractogram of the film was recorded by X-pert pro X-ray diffractometer operated at 45 kV, 30 mA at 0.01°/0.8 s in the 2θ range 20.005°-69.995° using CuK_α radiation (λ = 1.54056 Å). The UV-Vis spectrum was recorded by GBC-CINTRA 40 in the wavelength range 200-900 nm. The room temperature PL spectrum (27°C) was recorded by HR800 (Horiba Jobin Yvon) using Ar laser (λ = 514 nm), (focal length = 800 mm), grating (1800 grooves/mm) and CCD detector (1024 pixels). The elemental composition of the CdS thin film was estimated by EDAX analysis.

Fig. 1 — CdS thin film on glass-substrate

3. 1 Characterization using XRD

The XRD plot of the film before annealing [Fig. 2(a)] and after annealing [Fig. 2(b)] reveal coexistence of cubic and hexagonal phases (polymorphism) in the as-deposited film while on annealing there is a complete structural transformation to hexagonal phase with improved crystallinity. The XRD-data is given in Table 1.

The grain-size in the film is estimated using Scherrer formula:

$$D_c=\frac{K\lambda}{\beta\cos\theta} \quad \ldots(5)$$

where K is the Scherer's constant, λ is the wavelength of the X-ray, β is full-width at half-maximum (FWHM) in radians and θ is the Bragg angle. On annealing the film, calculated grain-size {(002) H reflection at 2θ = 26.375°} is found to be increased from 15.5 to 47.8 nm owing to grain-boundary diffusion.

3.2 Characterization using UV-VIS spectrophotometer

The transmission spectrum of the CdS thin film before annealing [Fig. 3(a)] and after annealing [Fig. 3(b)] are as shown. Figure 3(a) shows 40% transmittance (T) for wavelength above 500 nm and more than 50% above 750 nm with the absorption edge at 478 nm. The optical transmittance at 500 nm

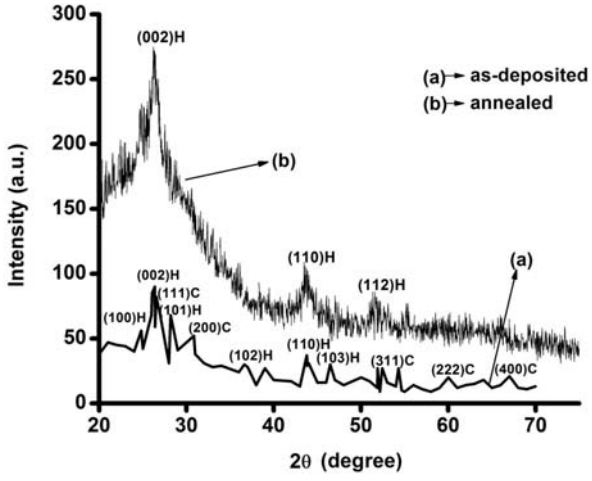

Fig. 2 — XRD patterns of as-deposited (a) and annealed (b) CdS thin film

Table1 — Structural data of as-deposited and annealed CdS thin film

CdS (hexagonal)				CdS (cubic)		
(h k l)	d_{std} (nm) (JCPDS 6-314)	d_{exp} (nm) (as- deposited)	d_{exp} (nm) (annealed)	(h k l)	d_{std} (nm) (JCPDS 10-454)	d_{exp} (nm) (as- deposited)
(1 0 0)	0.3583	0.3583	-	(1 1 1)	0.336	0.3355
(0 0 2)	0.3357	0.3376	0.3379	(2 0 0)	0.290	0.2896
(1 0 1)	0.316	0.3163	-	(3 1 1)	0.175	0.1742
(1 0 2)	0.245	0.2451	-	(2 2 2)	0.168	0.1687
(1 1 0)	0.2068	0.2065	0.2066	(4 0 0)	0.1453	0.1452
(1 0 3)	0.1898	0.1951	-			
(1 1 2)	0.1761		0.177			

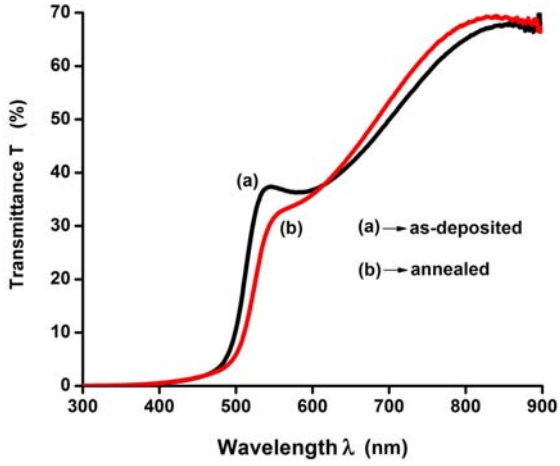

Fig. 3 — Optical transmission (T) spectra of as-deposited (a) and annealed (b) CdS thin film

is slightly lesser in Fig. 3(b) than in Fig. 3(a). The shift of the absorption edge towards lower energy is due to the structural change resulting from annealing.

The absorption coefficient α (Eq. 6) and extinction coefficient *k* (Eq. 7) are calculated:

$$\alpha = \frac{-\ln(T)}{t} \qquad \ldots(6)$$

$$k = \alpha\lambda / 4\pi \qquad \ldots(7)$$

where T is transmittance, t is film-thickness and λ is wavelength.

The variations of α with λ (Fig. 4) and k with λ (Fig. 5) for the film before and after annealing are as shown.

The optical band gap is calculated using the formula:

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \qquad \ldots(8)$$

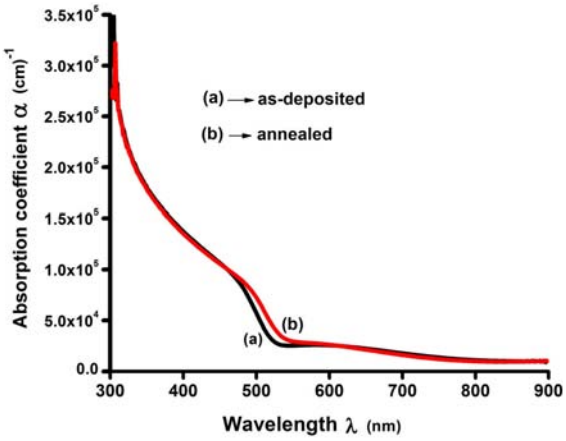

Fig. 4 — Plot of absorption coefficient (α) vs wavelength (λ) of as-deposited (a) and annealed (b) CdS thin film

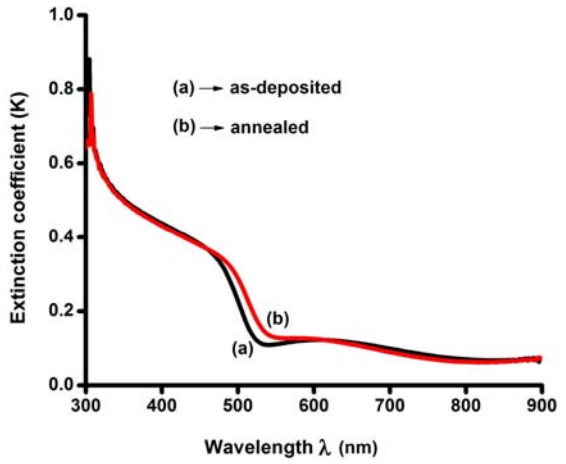

Fig. 5 — Plot of extinction coefficient (*k*) versus wavelength (λ) of (a) as-deposited and (b) annealed CdS thin film

where $h\nu$ is the photon energy, E_g the optical band gap of the material and A is a constant.

The linear portion of the plot $(\alpha h\nu)^2$ versus $h\nu$ extrapolated for $(\alpha h\nu)^2 = 0$ gives a band gap value of

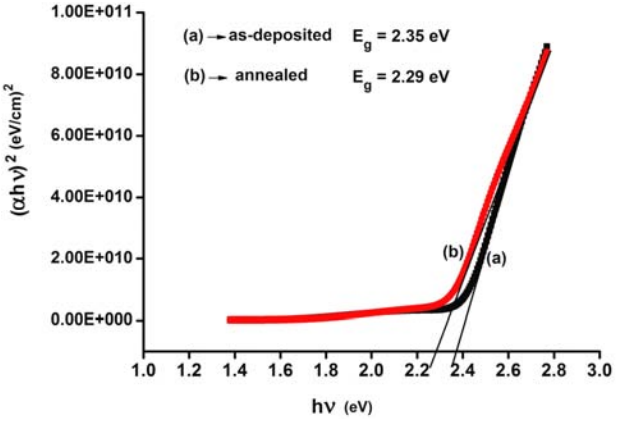

Fig. 6 — Variation of $(\alpha h\nu)^2$ versus $h\nu$ of as-deposited (a) and annealed (b) CdS thin film

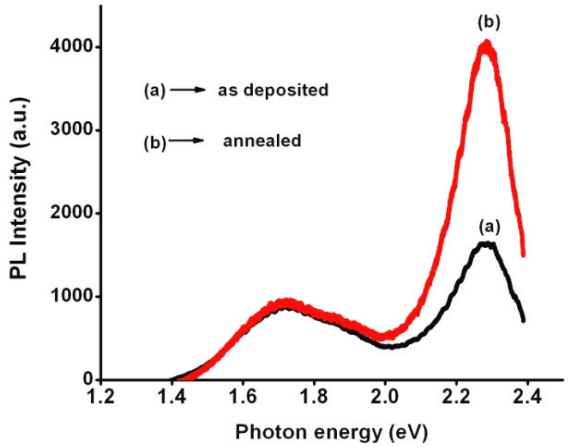

Fig. 7 — Photoluminescence spectra of as-deposited (a) and annealed (b) CdS thin film

2.35 eV before annealing and 2.29 eV after annealing (Fig. 6). A decrease in the band gap due to annealing is noticeable.

3.3 Photoluminescence analysis

The room temperature PL spectrum of the CdS thin film before and after annealing (Fig. 7) shows two broad emission bands at 2.28 eV and 1.72 eV. The green band at 2.28 eV is due to donor-acceptor transition. The red band at 1.72 eV is due to the transition of the electrons from deep level to valence band[17]. The intensity of the green emission is almost doubled on annealing while for the red emission there is a slight enhancement.

3.4 EDAX

The elemental composition of the CdS thin film before annealing (Fig. 8) and after annealing (Fig. 9) analysed using EDAX reveals peaks corresponding to

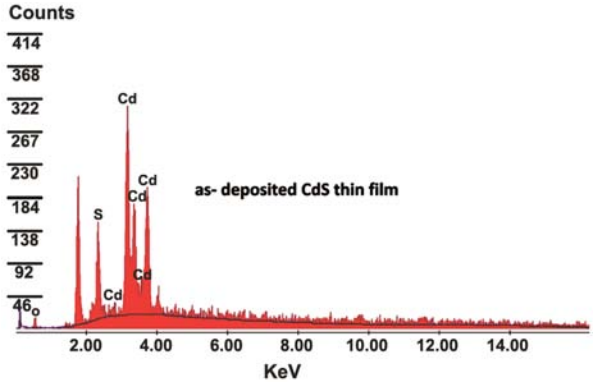

Fig. 8 — EDAX spectrum of as-deposited CdS thin film

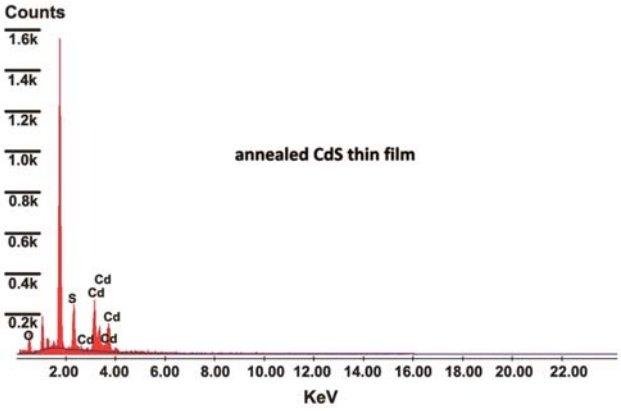

Fig. 9 — EDAX spectrum of annealed CdS thin film

cadmium and sulphur with appreciable intensity of cadmium peak and sulphur peak. The oxygen-peak is due to substrate (SiO_2). The average atomic percentage ratio is Cd:S = 60.45:29.13 (~2:1) before annealing. After annealing stoichiometric CdS thin film with ratio Cd:S =19.01:17.88 (~1:1) is obtained.

4 Conclusions

The growth condition with bath- temperature 80°C, *p*H ~11 and orientation of the substrate in the bath yielded CdS thin film with good adherence, uniform grain-size and good surface-coverage. The structural characterization reveals good degree of crystallization in the mixed-phases (hexagonal and cubic) that transformed to pure hexagonal phase on annealing with improved crystallinity. The optical study reveals a small reduction in the band gap value for the annealed film. On annealing, the thin film resulted in an appreciable increase in the intensity of the green band luminescence of the photoluminescence spectrum. EDAX analysis of the film reveals that on annealing, the film becomes almost stoichiometric.

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