Effect of annealing on the stoichiometry of CdS films deposited by SILAR technique

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Good quality CdS films were deposited on glass substrates by the simple and inexpensive SILAR (Successive Ionic Layer Adsorption and Reaction) technique from aqueous solutions having different S:Cd ratios (1:1, 3:1, 5:1 and 7:1). The annealing induced changes in the structural, surface morphological, elemental and optical properties were studied and reported. The X-ray diffraction studies revealed that a transformation from cubic or mixed phase to the pure hexagonal phase was caused by the annealing process at 350 °C and the degree of crystallinity was enhanced very much due to annealing. The recrystallization induced by the annealing process improved the S/Cd ratio in the films and thereby made the films to acquire good stoichiometry suitable for photovoltaic applications. The annealed films were found to have better transmittance (>85 %) in the visible region and enhanced optical band gap (2.50 eV).

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1. Introduction

Cadmium sulphide (CdS) is an n-type semiconductor with a direct wide band gap (E_g = 2.42 eV) and optical absorption suitable for solar cells. CdS has shown great potential in the manufacture of various devices such as photo detectors, piezo-electric transducers, bolometer, display panels, LEDs and photovoltaic cells [1-3]. It is one among the most promising candidates for photo electrochemical applications due to its higher conduction band edge positions for reduction/oxidation of water, high optical absorption and high electron affinity. The polycrystalline films of CdS can be prepared by different methods such as sputtering [4], photo chemical method [5], flash evaporation [6], ion layer gas reaction (ILGAR) [7], laser ablation [8], spray pyrolysis [9], spin coating [10] precipitation method [11], ultrasound-assisted method [12], flux method [13], thermal vacuum evaporation [14], chemical bath deposition (CBD) [15-17] and SILAR (successive ionic layer adsorption and reaction) [18, 19] etc. In the present study, CdS thin film deposition is carried out by the SILAR technique as it is simple, attractive and less expensive when compared with other methods. SILAR technique was introduced by Nicolau in the mid 1980's [18]. This method has been employed widely to grow selected II-VI compounds, especially CdS and ZnS. It is an aqueous solution technique based on sequential reactions at the substrate-solution interface for the deposition of thin films.

The main advantage of SILAR technique is easy control over the growth rate through the various parameters viz., time of deposition, number of immersions, solution concentration, bath temperature and pH of the precursor solution [19].

In the present contribution, CdS films were deposited on glass substrates from starting solutions having S:Cd ratios 1:1, 3:1, 5:1 and 7:1. In the utilization of the CdS films for electro-optical applications, crystalline quality of the films plays an important role [20]. Many researchers [21-23] reported that thermal annealing leads to the improvement in the crystalline quality of the films by the removal of random strain, which can change its electrical resistivity. Eventhough, several reports on the annealing effect on various properties of CdS film are available in the literature, the stoichiometry related discussions are hardly available to the best of our knowledge. Keeping the above observations in mind, in the present study, the stoichiometry related properties along with the structural, optical and morphological characteristics of annealed films were studied in detail and compared with that of their as-deposited counterparts.

2. Materials and methods

CdS films were fabricated by SILAR method from aqueous solutions having S:Cd ratios 1:1, 3:1, 5:1 and 7:1. Highly pure $CdCl_2.H_2O$ and H_2NCSNH_2 were used as sources for cadmium and sulphur ions respectively. Four different sets of films were prepared by keeping the concentration of $CdCl_2.H_2O$ solution as 0.1 M and that of H_2NCSNH_2 as 0.1, 0.3, 0.5 and 0.7 M. The cleaned glass substrate was immersed in 0.1 M cadmium chloride solution for 15 s to get cadmium ions adsorbed on the substrate. To remove loosely bound Cd^{2+} ions, the substrate was rinsed in doubly de-ionized water for 10 s. Then the substrate was immersed in thiourea solution for 15 s where S^{2-} ions react with the pre-adsorbed Cd^{2+} ions to form CdS thin film on the substrate. Again the substrate was rinsed in doubly deionized water for 10 s to remove unreacted S^{2-} ions and loosely bound CdS material from the substrate.

The number of cycles of immersion was varied from 100 to 50 to keep the thickness constant (450-500 nm). The temperature of the solutions and de-ionized water was maintained at 80 °C. In order to confirm the reproducibility of the films, several sets of films were fabricated by employing identical process conditions. After characterization, one set of films were annealed at 350 °C for 2 hours and again characterized and the obtained results were compared with that of their as-deposited counterparts. This annealing temperature was selected for the present study, because, in CdS films deposited on glass substrates, sulphur evaporates at higher temperatures ($T \geq 450$ °C) generally [24]. The adhesive nature of the films with the glass substrate was examined using the peel test and it was found that the films have good adhesion with the surface of the substrates both before and after annealing.

The as-deposited and annealed films were structurally characterized by X-ray diffraction in the range of diffraction angle $20° \leq 2\theta \leq 80°$. The diffraction patterns were recorded using X–ray diffractometer (PANalytical - PW 340/60 X' pert PRO) which was operated at 40 kV and 30 mA with X-ray source of CuK_α radiation having wavelength 1.5406 Å. Surface morphological images were observed using a scanning electron microscope (SEM) (HITACHI S-3000 H) and the quantitative analysis of the films were carried out using energy dispersive X-ray analysis (EDAX). Transmission spectra in the range of 300-1100 nm were recorded using UV-Vis-NIR double beam spectrophotometer (Perkin Elmer LAMBDA-35).

3. Results and discussion

Film formation and reaction mechanism

In the cadmium precursor solution, cadmium chloride dissolves in water and releases Cd^{2+} according to the following relation.

$$CdCl_2 + 4(NH_3) \rightarrow Cd\,(NH_3)_4\,Cl_2 \qquad (1)$$

The cadmium compound ion is then dissociated as follows

$$[Cd\,(NH_3)_4]^{2+} \rightarrow Cd^{2+} + 4NH_3 \qquad (2)$$

The cadmium ions (Cd^{2+}) are adsorbed on the glass substrate when it is immersed into cadmium chloride solution. The un-adsorbed Cd^{2+} ions are separated out by rinsing the substrate in doubly deionized water. Ammonia hydrolyzes in water to give OH^- [25] as follows;

$$NH_3 + H_2O \rightarrow [NH_4]^+ + [OH]^- \qquad (3)$$

$$Cd^{2+} + 2OH^- \rightarrow Cd\,(OH)_2 \qquad (4)$$

The thiourea hydrolyzes in alkaline solution to give S^{2-} ion as given below

$$(NH_2)_2\,CS + 2[OH]^- \rightarrow [HS]^- + H_2O + CH_2N_2 \qquad (5)$$

$$[HS]^- + [OH]^- \rightarrow S^{2-} + H_2O \qquad (6)$$

$$[Cd\,(NH_3)_4]^{2+} + S^{2-} \rightarrow CdS + 4NH_3 \qquad (7)$$

After immersion of such substrate in S^{2-} ion containing solution, S^{2-} ions react with pre-adsorbed Cd^{2+} to form a layer of CdS which can be written as

$$Cd^{2+} + S^{2-} \rightarrow CdS \qquad (8)$$

Such cycles are repeated required number of times to obtain continuous CdS thin film of desired thickness.

Structural studies

The X-ray diffraction patterns of the as-deposited and annealed CdS films deposited by the SILAR technique are given in Fig. 1 (a and b) respectively. In this study, all the as-deposited films exhibit a strong single peak at $2\theta = 26.7°$. This peak at $\pm 26°(2\theta)$ corresponds to the hexagonal (wurtzite) and the cubic (zinc blende) phases of CdS thin films [26]. The strong preferred orientation is due to the controlled nucleation process associated with the low deposition rate [27]. This strong diffraction peak can be assigned to the (002) plane of hexagonal or the (111) plane of cubic CdS. Therefore it is difficult to elucidate whether the film is purely hexagonal or purely cubic or a mixture of these two phases. But in the case of annealed film deposited from starting solution having S:Cd = 1:1, a polycrystalline structure is observed with peaks at 2θ = 24.81°, 26.49°, 28.18°, 36.63°, 43.69°, 47.83° and 51.85° corresponding to (100), (002), (101), (102), (110), (103) and (112) planes of hexagonal phase respectively. As all the above mentioned peaks are exactly matched with the hexagonal (wurtzite) structure of the CdS (JCPDS 06-0314), we can strongly conclude that there is a clear phase transformation from the cubic or mixed phase to the pure hexagonal phase. Similar results were reported by Metin et al. [28] for annealed CdS films deposited by CBD technique. Metin et al. [29] reported that the hexagonal phase became dominant with the increase in the annealing temperature and at T>623 K, the structure became pure stable hexagonal one. The phase transformation from cubic to hexagonal was observed for the chemically deposited CdS films by many other researchers also [30-34].

In the other three annealed samples prepared from starting solutions having S:Cd ratio 3:1, 5:1 and 7:1 also, some of the above mentioned peaks corresponding to the hexagonal phase were observed (Fig. 1b) confirming the phase transformation. It is found that, in the case of 1:1

film, (101) peak has emerged as predominant over (002) peak unlike in all other cases. The EDS quantitative analysis revealed that only in the case of 1:1 films, the S:Cd ratio is very much less than unity (0.8325), indicating the presence of higher sulphur deficiency. Hence, we can conclude that the sulphur deficiency plays an influential role in determining the structure after annealing. This conclusion is strongly supported by the variation in the grain size of the 1:1 film before and after annealing. In this case, the grain size increases nearly six times (11.9 nm to 66.3 nm) after annealing, but in all the other samples in which the sulphur deficiency is very low or absent, the increase in grain size is not appreciable as shown in the Table 1.

The intensity of the diffraction peak corresponding to the preferential orientation is gradually increased as the S:Cd ratio in the starting solution is increased. This trend is true for both as-deposited and annealed films. Moreover, the intensity values in the case of annealed films are larger when compared with that of the as-deposited films indicating the better crystallinity of the annealed films. It is found that the annealing process causes a left shift in the diffraction angle (2θ) of the preferential orientation peak in all the films irrespective of the S:Cd ratio as shown in Table 1. This left shift in 2θ value is remarkable in all the films confirming the recrystallization of the films during annealing.

The increase in the crystallinity of the films with the increase in S:Cd ratio in the starting solution was also evidenced by the gradual decrease in the full-width-half-maximum (FWHM) value and the resultant enhancement in the crystallite size. The crystallite size was calculated using Debye Scherrer's formula D = 0.94λ/β cosθ where β is the full-width at half-maximum (FWHM), D is the grain size, λ is the wavelength of X-ray (1.5406 Å) and θ is the Bragg angle [35]. The lattice constant 'a' for the cubic structure in the case of as-deposited films and the lattice constants a and c for the hexagonal structure in the case of annealed films were calculated using the following formulae respectively:

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \tag{9}$$

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2+k^2+l^2}{a^2} + \frac{l^2}{c^2} \tag{10}$$

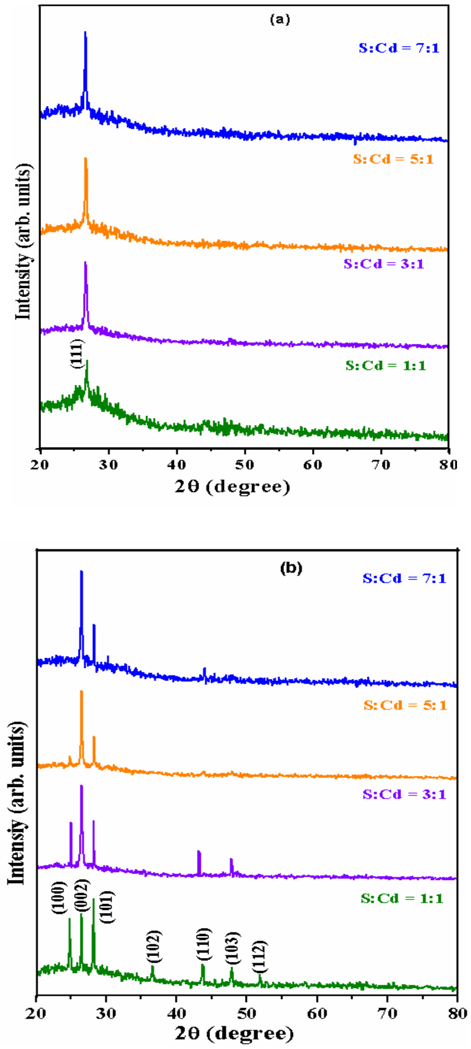


Fig. 1. X-ray diffraction patterns of the (a) as-deposited and (b) annealed CdS films.

Table 1. Crystallite size (D) and diffraction angle (2θ) of the CdS films.

	As-deposited		Annealed	
S:Cd ratio in the starting solutions (*M*)	D (*nm*)	Diffraction angle of (111) peak 2 θ (*degree*)	D (*nm*)	Diffraction angle of (111) peak 2 θ (*degree*)
1:1	11.9	26.652	66.2	26.493
3:1	24.9	26.675	31.2	26.520
5:1	29.4	26.766	36.2	26.523
7:1	33.0	26.682	33.2	26.505

The lattice constant 'a' for the as-deposited cubic structured CdS film (S:Cd = 1:1) is 5.764 Å and the 'a' and 'c' of the annealed hexagonal CdS (S:Cd = 1:1) film are found to be 4.223 Å and 6.720 Å respectively.

Morphological characterization

Scanning electron micrographs of the as-deposited and the annealed films are shown in Fig. 2 and Fig. 3 respectively. It is seen that the surface of the as-deposited films have spherical grains and it is obvious that the diameter decreases (from 120 to 50 nm) with the increase in the S:Cd ratio in the starting solution. But, the XRD results showed that the crystallite size increases with the increase in S:Cd ratio. These results revealed that in the as-deposited films, the agglomeration of crystallites is substantial when S:Cd ratio is lesser. Interestingly, a reverse phenomenon is observed in the case of annealed films in which the grain size increases as the S:Cd ratio increases. Moreover, the shape of the grains is also different in annealed films. The surface of the annealed films consists of a mixture of ellipsoidal, needle and spherical shaped grains and the size is found to be varied from 80 to 350 nm. All these changes in the surface morphology are attributed to the recrystallization caused by the annealing process.

Elemental analysis

The EDAX spectra of the as-deposited and the annealed CdS films with the inset tables showing the weight and atomic compositions of cadmium and sulphur are presented in Fig. 4 and Fig. 5 respectively. The other elements (Ca, O, Na and Si) which are supposed to be not expected in the deposited films may be resulted from the glass substrates. The S/Cd ratio in the as-deposited film prepared from the starting solutions having S:Cd ratio 1:1 is only 0.8325 indicating that there is ~17% sulphur deficiency in the film. But the S/Cd ratio in the film gradually increases (from 0.8325 to 1.0508) as the sulphur cadmium ratio in the starting solution increases as given in the Table 2. It is found that near stoichiometry is reached when the S/Cd ratio in the starting solution is 5:1.

Martinez et al. [36] reported that in the case of CBD films, nearly 20% sulphur deficiency exists even when the S:Cd ratio in the starting solution is increased to 100:1. But in SILAR method, in the present study, we obtained near stoichiometric CdS films from the solutions containing S:Cd ratio 5:1 and 7:1. These results clearly showed that the number of available S^{2-} ions in the anionic solution to form CdS by combining with Cd^{2+} ions already adsorbed on the surface of the substrate is sufficient even in the last dippings. But, in the case of 1:1 film it is not so and hence resulted sulphur deficiency in the deposited films. But after annealing, the S/Cd ratio in the case of 1:1 film increases from 0.8325 to 0.9271, indicating a decrease in the sulphur deficiency from 17% to 7%.

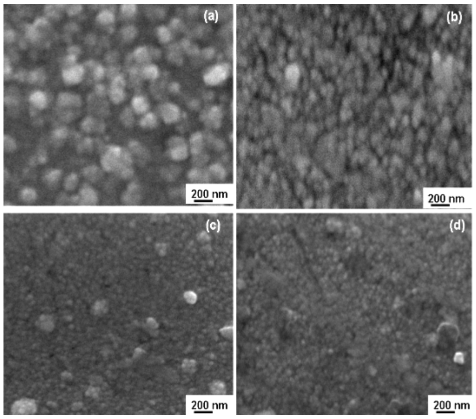


Fig. 2. SEM images of as-deposited CdS films deposited using starting solutions having S:Cd ratio (a) 1:1 (b) 3:1 (c) 5:1 and (d) 7:1.

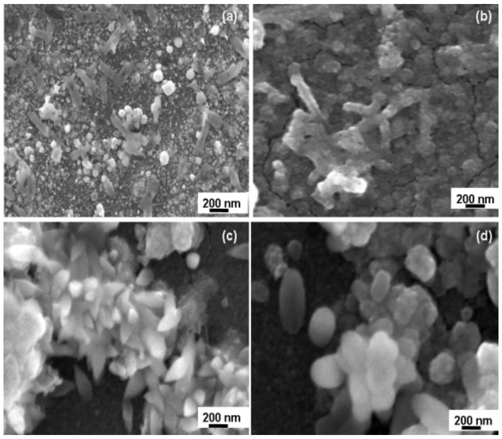
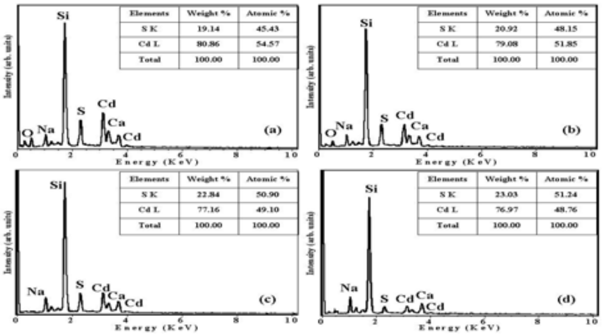


Fig. 3. SEM images of annealed CdS films prepared using starting solutions having S:Cd ratio (a) 1:1 (b) 3:1 (c) 5:1 and (d) 7:1.

This decrease in sulphur deficiency in annealed films may be attributed to the recrystallization due to annealing which causes the movement of sulphur atoms in the deeper layers to the surface layers. Since EDAX measurements give the atomic proportions only in the surface and near surface layers, one can easily understand the above mentioned discussions. Similarly, in the 3:1 film, the S/Cd ratio increases from 0.9286 to 0.9616 after annealing. But in 5:1 and 7:1 films, the recrystallization due to annealing does not have much influence on the S/Cd ratio as the near stoichiometry is already present in the as-deposited films themselves. Thus the quantitative studies of EDAX results clearly showed that the annealing process increased the S/Cd ratio in the films and resulting in good stoichiometric CdS films. Liu et al. [37] reported that at near stoichiometry, CdS films have less resistivity values suitable for photovoltaic applications. Therefore, we can conclude that the thermal annealing process induced desirable changes in the photovoltaic related properties of the CdS films.



(a)

Elements	Weight %	Atomic %
S K	19.14	45.43
Cd L	80.86	54.57
Total	100.00	100.00

(b)

Elements	Weight %	Atomic %
S K	20.92	48.15
Cd L	79.08	51.85
Total	100.00	100.00

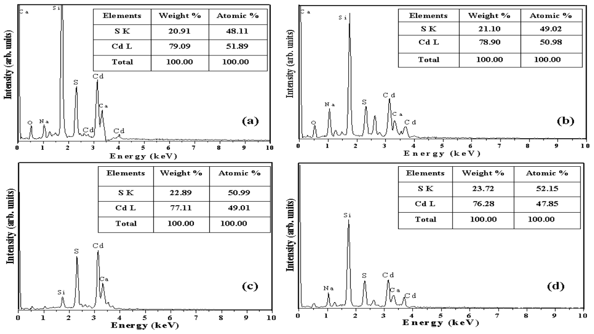
(c)

Elements	Weight %	Atomic %
S K	22.84	50.90
Cd L	77.16	49.10
Total	100.00	100.00

(d)

Elements	Weight %	Atomic %
S K	23.03	51.24
Cd L	76.97	48.76
Total	100.00	100.00

Fig. 4. EDS spectra of as-deposited CdS films prepared using starting solutions having S:Cd ratio (a) 1:1 (b) 3:1 (c) 5:1 and (d) 7:1.



(a)

Elements	Weight %	Atomic %
S K	20.91	48.11
Cd L	79.09	51.89
Total	100.00	100.00

(b)

Elements	Weight %	Atomic %
S K	21.10	49.02
Cd L	78.90	50.98
Total	100.00	100.00

(c)

Elements	Weight %	Atomic %
S K	22.89	50.99
Cd L	77.11	49.01
Total	100.00	100.00

(d)

Elements	Weight %	Atomic %
S K	23.72	52.15
Cd L	76.28	47.85
Total	100.00	100.00

Fig. 5. EDS spectra of annealed CdS films deposited using starting solutions having S:Cd ratio (a) 1:1 (b) 3:1 (c) 5:1 and (d) 7:1.

Table 2. S/Cd ratio in the as-deposited and annealed films.

S:Cd ratio in the starting solutions (*M*)	S/Cd atomic composition ratio in the films		Band gap (E_g) *eV*	
	as-deposited	annealed	as-deposited	annealed
1:1	0.8325	0.9271	2.35	2.38
3:1	0.9286	0.9616	2.39	2.42
5:1	1.0366	1.0404	2.40	2.46
7:1	1.0508	1.0899	2.45	2.50

Optical studies

The optical transmission spectra of the as-deposited and annealed CdS films in the range of 300-1100 nm are recorded and shown in Fig. 6. The band gap of the material can be determined by the rapid fall in the transmission. The sharp absorption edge of the spectra indicates the good crystallinity of the films. The average transmittance in the visible range is found to be in the range of 75-85% for as-deposited films and this value increases slightly (78-90%) after annealing.

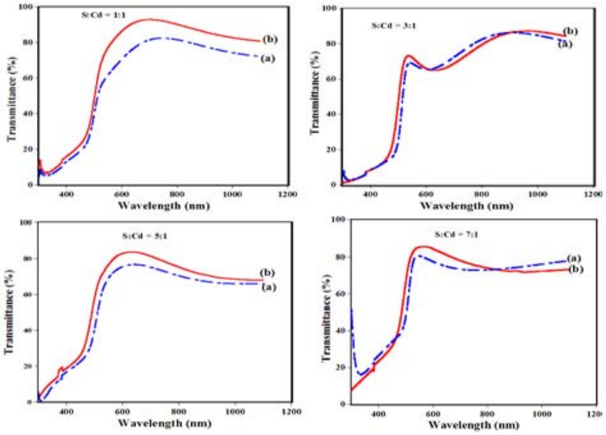


Fig. 6. Transmittance spectra of (a) as-deposited and (b) annealed CdS films.

The absorption coefficient (α) of films for various wavelengths can be calculated from the transmittance (T) values by using Lambert's law $\alpha = \ln(1/T)/t$ where t is the thickness of the film. Since CdS is a direct band gap material, the variation in α with hν is of the form $\alpha = A(h\nu - E_g)^{n/2}$ where A is a constant which is connected with the effective mass, E_g is the band gap and n is a constant which is equal to one. The transmittance of the annealed films is found to increased in all the cases irrespective of the S:Cd in the starting solution. The relative improvments in the transmittance are larger at shorter wavelengths. It is obvious from the Fig. 6 that, there is a blue shift in the absorption edge due to annealing in all cases. This result clearly indicates that the band gap increases due to annealing in all the S:Cd ratios. This increase in E_g can be attributed to the improvement in the crystallinity of the films.

The direct band gap values are determined from the intercept of the extrapolated straight-line portion of the $(\alpha h\nu)^2$ vs $(h\nu)$ plot (Tauc's plot) on the hν axis. The band gap of the as-deposited as well as the annealed CdS films is found to increase with the increase in S:Cd ratio in the starting solution. The estimated E_g values for the as-deposited and the annealed films are presented in Table 2. These values are well agreed with the earlier reports [38-40].

4. Conclusions

CdS films having good adherence with glass substrates were fabricated using the SILAR technique. It was found that the thermal annealing at 350 °C caused a phase transformation from cubic or mixed phase to the pure hexagonal phase and the annealing process improved the crystalline quality of all the films irrespective of the S:Cd ratio in the starting solution. It is also found that the annealing process induced the recrystallization of the films which resulted enhancement in the S/Cd ratio in the films which in turn leads to the good stoichiometry of the films. The increase in the optical transmittance, optical band gap and the better stoichiometry of the films resulted from annealing make these films suitable for photovoltaic and optoelectronic applications.

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