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Photovoltaic properties of nanocrystalline CdS films deposited by SILAR and CBD techniques—a comparative study

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Abstract CdS films were fabricated using Successive Ionic Layer Adsorption and Reaction (SILAR) technique from starting solutions having S:Cd ratio 1:1, 3:1, 5:1 and 7:1 and their structural, surface morphological and optical properties were investigated and compared with that of their chemical bath deposited counterparts. The X-ray diffraction profiles showed that the films have cubic crystal structure with preferential orientation along the (111) plane and the intensity of the (111) plane increases for both the techniques as the S:Cd ratio increases. The energy dispersive X-ray analysis revealed that for SILAR deposited films, the S/Cd ratio in the sample increases from 0.8308 (for S:Cd 1:1) to 1.04 (for S:Cd 7:1) as the molar concentration of sulphur in the starting solution increases. But for CBD films, the S/Cd is only ~0.80 for all concentrations of sulphur in the starting solution. The optical band gap increases with the increase in S:Cd ratio in the starting solution in both the techniques.

1 Introduction

Cadmium sulfide (CdS) is one of the promising II-VI semiconductor materials [1] for use in solar cell devices, thin film transistors for flat panel displays, optical filters, photo-detectors and gas sensors. CdS is an n-type semiconductor which has direct band gap ($E_g = 2.42$ eV) and optical absorption suitable for solar cells [2]. It has shown much promise as an effective sensitizer because of its suitable band gap, long lifetime and important optical properties [3]. The fabrication of CdS films has become increasingly important in recent years, since CdS and its traditional p-type partner CdTe are leading and very promising materials for the development of cost effective and reliable photovoltaics [4]. CdS films have been prepared by various techniques such as vacuum evaporation, chemical bath deposition (CBD) [5], successive ionic layer adsorption and reaction (SILAR), aerosol jet deposition, spray pyrolysis etc. [6, 7]. Among these, SILAR and CBD are simple, convenient and low-cost techniques for large area coatings. Recent attention in chemical solution deposition of CdS nanocrystals [8–10], CdS nanotubes [11] and CdS nanowires [12] arise from their potential use in new optical materials such as sensitizers of dye-sensitized solar cells [8, 9] and CdS nanorod superlattices [13]. In the present work, CdS films were fabricated using SILAR technique from starting solutions having S:Cd ratio 1:1, 3:1, 5:1 and 7:1 and their structural, surface morphological, elemental and optical properties are studied and compared with the properties of CBD CdS films prepared with the same deposition conditions. Eventhough, there are plenty

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of reports available on CBD-CdS films in the literature, the studies on CdS films deposited by SILAR technique are comparatively lesser. Moreover, the stoichiometry related discussions on SILAR deposited films are very scarce in the literature. Therefore, in the present study, the stoichiometric analysis on the basis of quantitative results of EDAX spectra of both the SILAR and CBD CdS films have been carried out in detail.

2 Materials and methods

CdS films were fabricated from aqueous solutions by SILAR and CBD methods having S:Cd ratios 1:1, 3:1, 5:1and 7:1. Highly pure $CdCl_2.H_2O$ and H_2NCSNH_2 were used as sources for cadmium and sulphur ions respectively in this study. The concentration of $CdCl_2$. H_2O is kept as 0.1 M and that of H_2NCSNH_2 is kept as 0.1, 0.3, 0.5 and 0.7 M. In the case of SILAR technique, the immersion times for cationic and anionic solutions are kept as 15 s. The number of cycles of immersion is kept as 50 for all S:Cd ratios for one set of films. For another set of films, to keep the thickness constant, (450–500 nm) the number of cycles of immersion is varied correspondingly. SILAR is one of the newest solution methods which is based on sequential reactions at the substrate-solution interface for the deposition of thin films. The experimental procedure for the CBD technique is given elsewhere [14]. Keeping the deposition times suitably, the thickness of the films is kept constant as in the case of SILAR technique. The thicknesses of the films were estimated using profilometer (Surftest SJ—301) and the values were compared with that obtained from the conventional weight gain method. Both the values were found to be comparable with each other.

X-ray 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. SEM images were obtained by employing scanning electron microscope (HITACHI S-3000 H). Elemental composition of the samples was determined by energy dispersive analysis of X-ray (EDAX) (Norton System Six, Thermo Electron Corporation, Instrument Super DRY II, USA). UV–Vis-NIR double beam spectrophotometer (LAMBDA- 35) is used to record transmission spectra in the range of 300–1100 nm.

3 Results and discussion

3.1 Growth rate

The thickness of the CdS film deposited by SILAR technique gradually increases when the S:Cd ratio in the starting solution increases as shown in Fig. 1. From this figure, we can see that there is a linear relationship between the S:Cd ratio in the starting solution and the thickness of the film. The reason for this increase in thickness with the increase in S:Cd ratio is the availability of increasing number of S^{2-} ions in the bath. In SILAR technique, the S^{2-} ions are not involved in undesirable homogeneous CdS formation unlike in the case of CBD technique as the cationic and the anionic solutions are kept in two different baths.

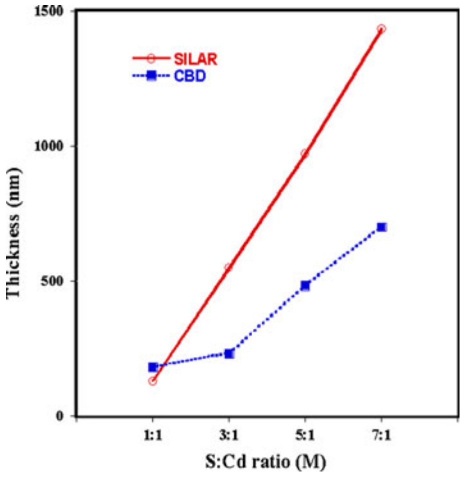

Fig. 1 Variation in thickness as a function of S:Cd ratio in the starting solution

3.2 Structural studies

The XRD patterns of the CdS films prepared by the SILAR and CBD techniques are shown in Fig. 2. In the case of SILAR technique, for all the films deposited from precursor solutions having the ratio of sulphur and cadmium (S:Cd) 1:1, 3:1, 5:1 and 7:1 only the peak at ±26 ° (2θ) corresponding to the hexagonal (002) plane (or cubic(111) plane) is observed. It is well known that CdS thin films have two crystalline modifications: the hexagonal (wurtzite) phase and the cubic (zincblende) phase. Both phases have peaks around ±26 ° (2θ) [15]. The actual phase for both the technique in the present study, is only cubic, since the phase transformation from cubic to hexagonal can take place only when the bath temperature is above 623 K [16–20].

In the case of SILAR CdS film deposited from starting solutions having S:Cd ratio 1:1, the intensity of the (111) peak is only 64.97 cps, but the intensity increases gradually as the S:Cd in the starting solution increases and attains a maximum of 301.9 cps for S:Cd = 7:1 as shown in the Table 1. It is reasonable to correlate these results with the quantitative results of EDS studies which showed that the S/Cd ratio of the 1:1 film is only 0.8308 and the value increases gradually with the increase in S:Cd in the starting

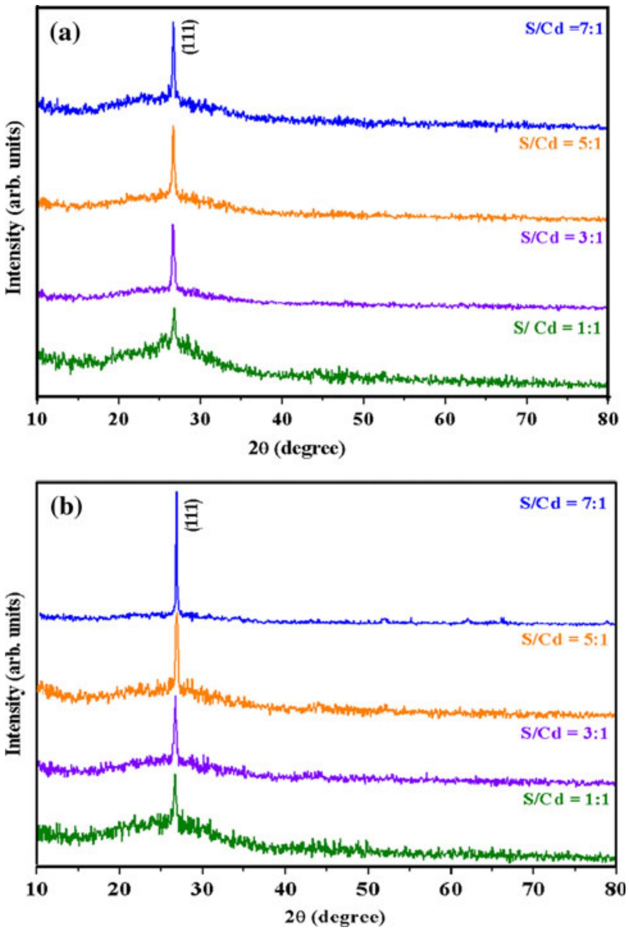

Fig. 2 XRD patterns of CdS films deposited by **a** SILAR and **b** CBD techniques

solution to attain 1.0467 for 7:1 film. Therefore one can conclude that the lower intensity of the preferential orientation peak and the comparatively higher amorphous nature of the 1:1 film may be due to the sulphur deficiency in this film and the improved crystalline nature of the other three films (3:1, 5:1 and 7:1) may be due to the better stoichiometry (Fig. 5) of these films when compared with the 1:1 film as discussed in sect. 3.4. This increase in crystallinity of the films with the increase in S:Cd ratio in the starting solution is also evidenced by the gradual decrease in the full- width-half- maximum (FWHM) value and the resultant enhancement in the crystallite size. These results are very much agreed with the reports of Liu et al. [21]. They reported that the intensity of the preferential orientation peak is higher for close stoichiometry (S/Cd=1) films when compared with the films having sulphur deficiency (S/Cd < 1) or sulphur excess (S/Cd>1).

The crystallite size is calculated using the Scherrer formula $D = 0.94\ \lambda/(\beta \cos\theta)$ where λ is the wavelength of the X-ray used (1.5406 Å), β is the full-width at half—maximum (FWHM) of the peak which has maximum intensity and θ is the Bragg angle. The calculated values (Table 1) showed that the crystallite size increases as the S:Cd ratio in the starting solution increases in both the techniques.

It is observed that in the case of CBD CdS films also, the preferential orientation is along the (111) plane. Further, it is found that for CBD CdS films also, the intensity of the preferential orientation increases as the S/Cd ratio increases, but only marginally unlike in the case of SILAR films in which the increase is appreciable.

The calculated structural parameters, crystallite size (D) and lattice constant a are summarized in Table 1. Lattice constant a is calculated using the relation

$$1/d^2 = \left(h^2 + hk + k^2\right)/a^2$$

where d is the interplanar spacing. The lesser values of a obtained in the case of CBD CdS films when compared with that of SILAR films and the standard (JCPDS 10-0454) values are due to the sulphur deficiency in the CBD CdS films.

3.3 Surface morphology

The SEM images of the CdS films deposited by the SILAR and CBD techniques are shown in Figs. 3 and 4. From the SEM images, the grain size values of the SILAR and CBD CdS films are estimated which are in the range of 30–50 nm and 40–60 nm respectively. The SEM images depict that the shape of the grains are similar in both the methods. The size and configuration of the grains of the chemically deposited chalcogenide films depend on many

Table 1 Structural parameters of CdS films

S:Cd	SILAR			CBD		
Molarity Ratio	Intensity cps	Crystallite size (D) × 10^{-9}m	*Lattice constant (Å) a	Intensity cps	Crystallite size (D) × 10^{-9} m	Lattice constant (Å) a
1:1	64.9	11.9	5.787	40.8	13.29	5.764
3:1	227.5	24.9	5.798	95.3	23.21	5.788
5:1	248.3	29.4	5.804	152.6	35.24	5.783
7:1	301.9	33.0	5.821	203.3	49.55	5.782

* Standard lattice constant value $a = 5.818$ Å, JCPDS card no 10-0454

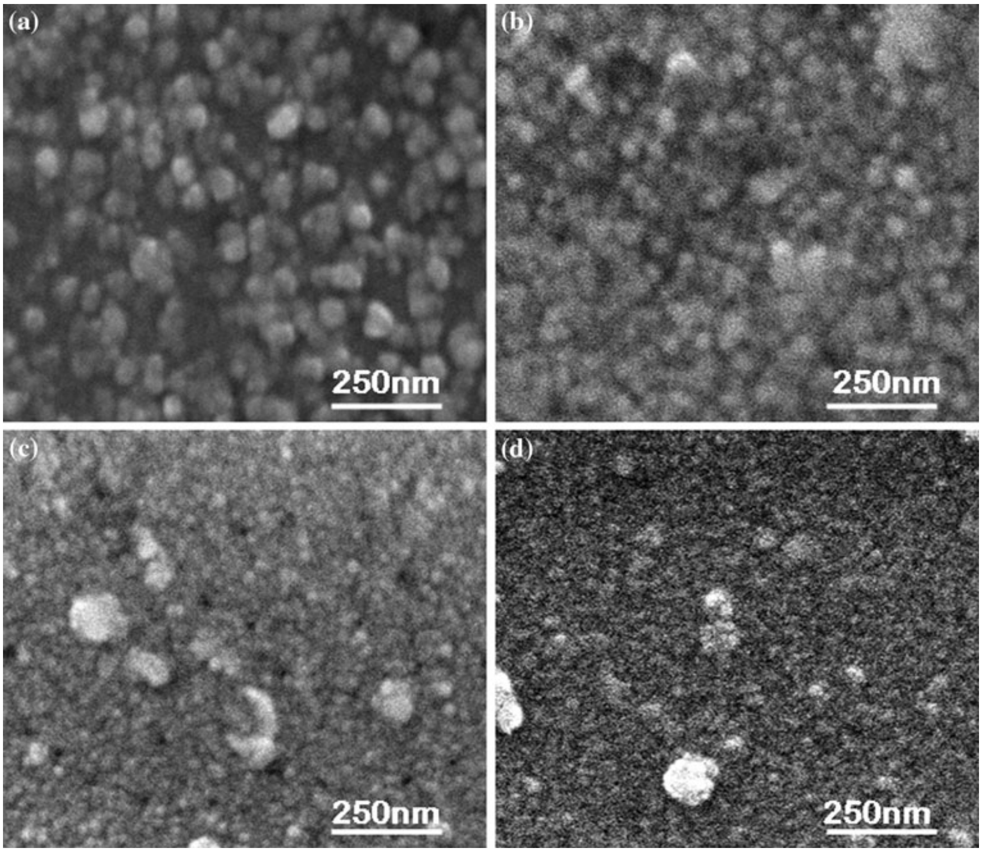

Fig. 3 SEM images of SILAR CdS films deposited using starting solutions having S/Cd ratio **a** 1:1 **b** 3:1 **c** 5:1 and **d** 7:1

parameters such as composition and temperature of the precursor solution, nature of the substrate etc. In the present study, eventhough both of the above mentioned parameters are kept as the same in both the SILAR and CBD films, there is a slight difference in grain size and packing density which may be due to the difference in the growth mechanism of the two methods. It has been demonstrated that the grain size and configuration are the direct consequences of the growth mechanism [22, 23].

3.4 Elemental analysis

The EDS spectra of the CdS films deposited by SILAR method from starting solutions having different S:Cd molar concentrations (1:1, 3:1, 5:1, 7:1) are given in Fig. 5, which shows that all the films contain the elements Cd and S as expected. The other elements (Ca, Si and Na) that are not expected to be in the deposited films may be resulted from the glass substrate [14, 24]. The weight and atomic compositions of sulphur and cadmium in the films are presented in Table 2. In earlier reports, for CBD, with different bath compositions of the thiourea and cadmium salt, Martinez et al. [25] observed that all the CBD–CdS samples are sulphur-poor (S/Cd ratio in the deposited films is lower than unity) even when the S:Cd ratio in the starting solution is 100:1. The sulphur deficiency may be due to the presence of oxygen in the films, because some oxygen ions can be substituted in the sulphur sites in the CdS lattice. This substitution is possible since the ionic radius of oxygen (O^{2-} −1.32 Å) is lesser than that of sulphur (S^{2-} −1.84 Å) [26]. For CBD films, the S/Cd is only ~0.80 for all concentrations of sulphur in the starting solution. But for the SILAR counterparts, S/Cd is 0.8308, only when the S/Cd ratio in the starting solution is 1:1 and for all the other molar concentrations (3:1, 5:1 and 7:1), the S/Cd in the samples is nearly equal to or greater than unity (0.9264 for 3:1, 1.03 for 5:1 and 1.04 for 7:1) indicating that there is very less or no sulphur deficiency unlike in the case of CBD CdS films. This discussion on the decrease in sulphur deficiency is also supported by the decrease in the amount of oxygen in the films shown by the EDS quantitative analysis (Fig. 5). From these results, we can conclude that the presence of sulphur deficiency in CdS films can be avoided by employing this SILAR technique. Liu et al. [27] reported that the minimal resistivity value was obtained for the close stoichiometric CdS films and hence we can say that SILAR deposited CdS films are more suitable for photovoltaic applications

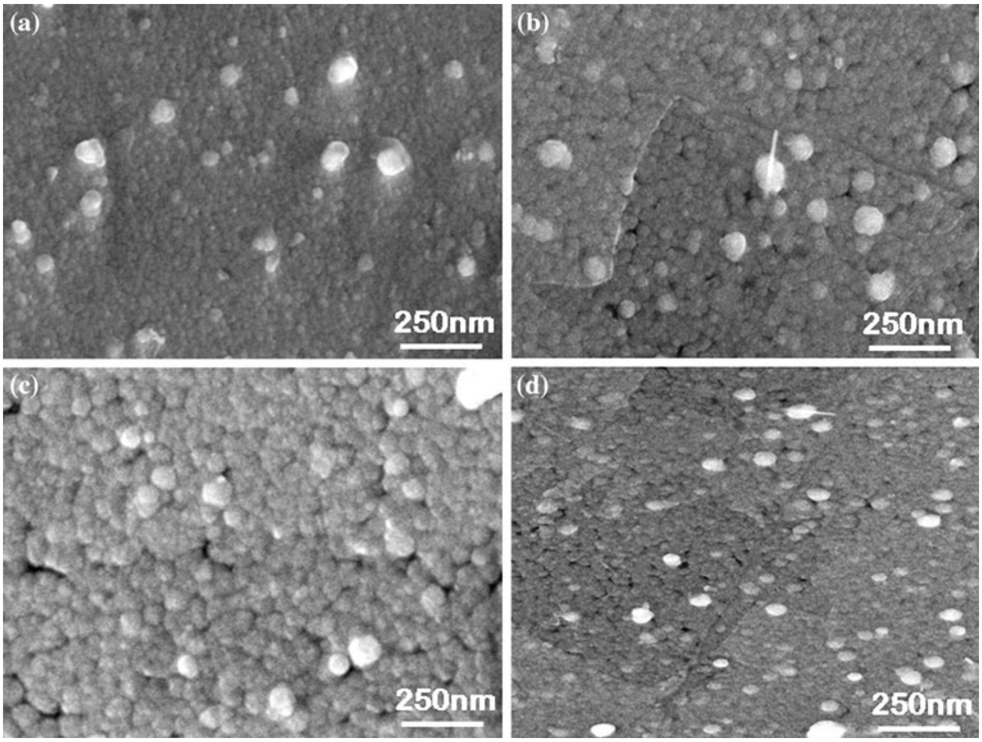

Fig. 4 SEM images of CBD CdS films deposited using starting solutions having S/Cd ratio **a** 1:1 **b** 3:1 **c** 5:1 and **d** 7:1

when compared with CBD CdS films because close stoichiometry can be obtained in SILAR films even for S:Cd ratio in the starting solution is 5:1, whereas in the case of CBD CdS films, stoichiometry is not achieved even when the S:Cd ratio of the starting solution is 100:1 [25].

The reason for the sulphur deficiency in the case of CBD is due to the process pattern and the growth mechanism. In CBD, as both cadmium and sulphur sources are kept together in the same bath, the probability for homogeneous formation of CdS is higher whereas in the case of SILAR technique, as the cationic and anionic solutions are kept in two different baths, the homogeneous CdS formation is avoided and only the heterogeneous reaction is taking place. Hence, in the SILAR technique, the available S^{2-} ions are effectively used for the heterogeneous formation of CdS films. But, in CBD, the available S^{2-} ions are involved in both heterogeneous and homogeneous reactions which results in the deficiency of sulphur in the deposited film.

3.5 Optical studies

The optical properties of the CdS films were investigated using the transmission and absorption spectra observed in the wavelength range 300–1,100 nm. The transmission spectra recorded for the SILAR and CBD CdS films are shown in Fig. 6. In the case of SILAR films, the transmittance in the visible range is only 65% for 1:1 film and the transmittance increases gradually up to 80% when S/Cd = 7:1. This increase in transmittance may be due to the enhancement in the crystallinity of the films and the consequent increase in the crystallite size of the films (Table 1). The same trend is observed in the CBD films also, but the minimum transmittance in this case is 70% as seen in Fig. 6b. Eventhough, in both the techniques the spectra show a sharp fall in transmission near the fundamental absorption edge, which is an identification of the good crystallinity [28] of the films, the extension of optical transmittance observed in the high energy region up to 330 nm is a strong evidence of some disorder effects or presence of amorphous components in the films [29].

The fundamental absorption which clearly shows itself by a rapid rise in absorption can be used to determine the band gap of materials. The absorption coefficient (α) can be calculated from the transmittance (T) values at the absorption edge from the Lambert law $\alpha = \ln(1/T)/t$. The variation of absorption coefficient against photon energy ($h\nu$) has the form of $\alpha = A(h\nu - E_g)^{n/2}$, where E_g is the band gap, ‘A’ is a constant related to the effective masses associated with the bands and n is a constant which is equal to one for a direct-gap material and four for an indirect-gap material.

To determine whether the CdS films deposited using the SILAR technique have direct or indirect band gap, $(\alpha h\nu)^2$ versus ($h\nu$) and $(\alpha h\nu)^{1/2}$ versus ($h\nu$) plots are drawn. Since better linearity is obtained in the $(\alpha h\nu)^2$ versus ($h\nu$) plots,

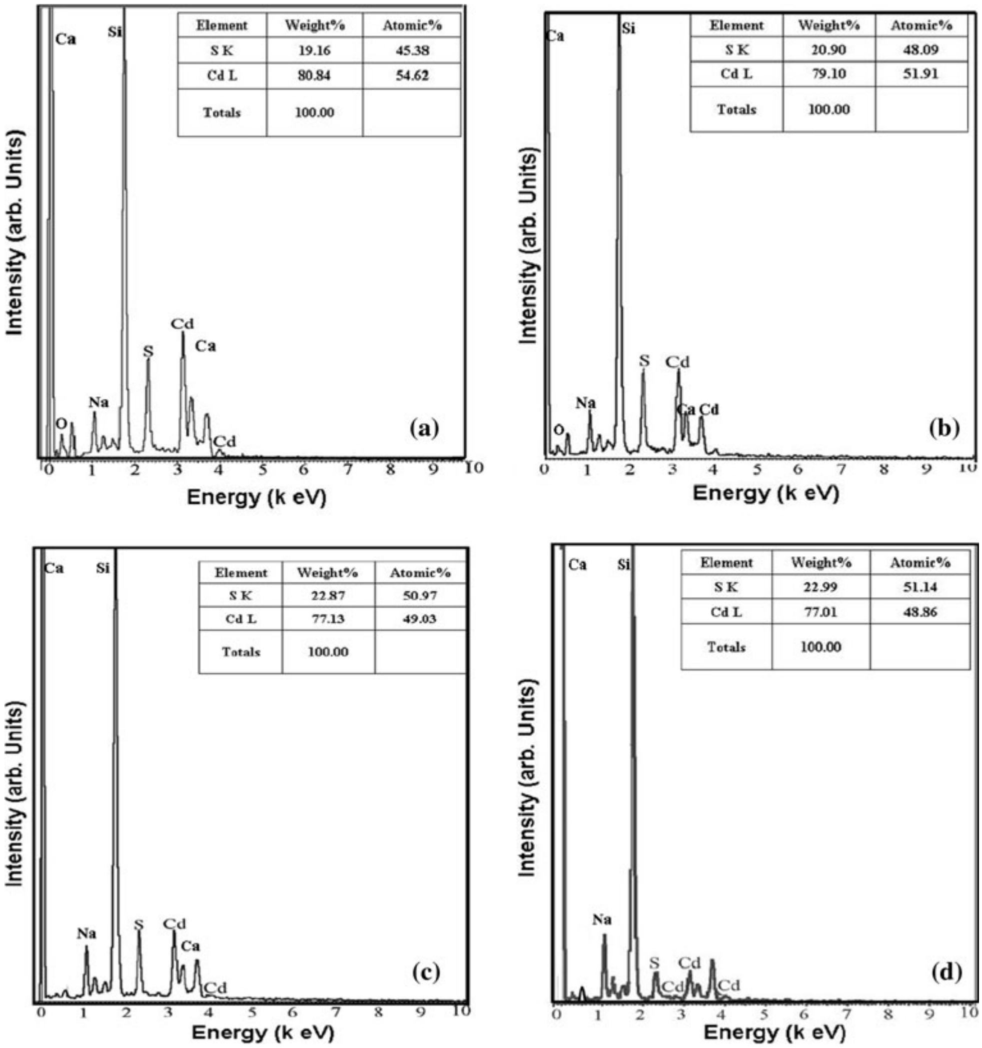

Fig. 5 EDS spectra of SILAR CdS films deposited using starting solutions having S/Cd ratio **a** 1:1 **b** 3:1 **c** 5:1 and **d** 7:1

Table 2 Quantitative analysis of SILAR and CBD films

S/Cd ratio in starting solution	Elemental composition				S/Cd composition ratio (at.%) in film
	Cd		S		
	wt. %	at.%	wt. %	at.%	
1:1	80.84	54.62	19.16	45.38	0.8308
3:1	79.10	51.91	20.90	48.09	0.9264
5:1	77.13	49.86	22.87	50.97	1.0396
7:1	77.01	48.86	22.99	51.14	1.0467

the direct band gap values are determined by extrapolating the linear portion of these plots to the energy axis. The band gap is found to increase from 2.35 to 2.46 eV as the S:Cd ratio in the starting solution increases in both the techniques [30]. The average optical transmittance and the estimated E_g values are presented in Table 3. The values are found to be comparable with the earlier reports [20, 31–34].

4 Conclusion

In the case of SILAR, the S/Cd ratio in the deposited films is less than unity (0.8308) when S:Cd in the starting solution is 1:1 and close stoichiometry is reached when S:Cd in the starting solution 5:1. But in the case of CBD CdS films, stoichiometry is not reached even when the S:Cd in the starting solution is 7:1. As CdS films with close

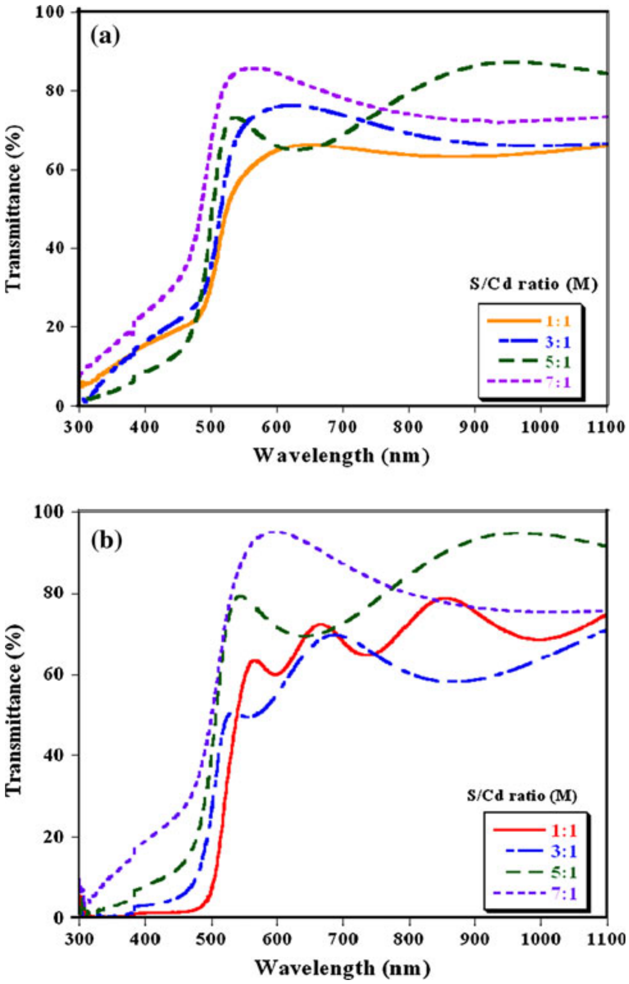

Fig. 6 Transmittance spectra of CdS films deposited by **a** SILAR and **b** CBD techniques

Table 3 Optical band gap of CdS films deposited by SILAR and CBD techniques

S/Cd molarity ratio	Band gap (eV)	
	SILAR	CBD
1:1	2.35	2.31
3:1	2.39	2.36
5:1	2.40	2.41
7:1	2.46	2.44

stoichiometry are good for solar cell applications, SILAR may be considered as better chemical method when compared with CBD. In both the techniques, it is found that the optical band gap increases with the increase in S:Cd ratio in the starting solution.

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