International Journal of Thin Film Science and Technology

Volume 4
Issue 2 *May 2015*

Article 6

2015

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http://dx.doi.org/10.12785/ijtfst/040206

Studies on Characterization of Cadmium Sulphide Thin Films Deposited by Chemical Bath Deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR) Method

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Received: 10 Nov. 2014, Revised: 2 Mar. 2015, Accepted: 3 Mar. 2015.
Published online: 1 May 2015.

Abstract: Cadmium Sulfide (CdS) were grown on glass substrate by chemical bath deposition (CBD) and Successive Ionic layer adsorption and reaction technique (SILAR) techniques. The structural, morphological and optical properties of the CBD deposited CdS thin films have been studied by varying the parameters such as concentration, pH and the deposition time. The ratio of S/Cd of the precursor was varied in order to have better understanding of the growth conditions. Similarly in SILAR method parameters such as concentration of cationic and ionic precursors, number of 125 immersion cycles, immersion time and pH of the solution were optimized. The films were characterized by X-ray diffraction, scanning electron microscope (SEM) and optical absorption measurements.The average crystallite size of the films deposited by CBD & SILAR technique is found to be 6.97nm and 5.56nm. The band gap is 2.48eV & 2.54eV for the CBD and SILAR method respectively. SEM images confirmed that the substrates are well covered with the deposited CdS layers without cracks or pinholes.

Keywords: Thin film, CBD, CdS , SILAR, Bandgap.

1 Introduction

In recent years, metal chalcogenide thin films of group II-VI semiconductors have received immense attention due to their wide applications in various fields of science and technology [1-5]. Cadmium Sulfide belonging to this group is regarded as one of the promising material for application in photovoltaic applications. CdS has a wide band gap which varies between 2.1 to 2.6 eV depending on the composition due to which it finds various applications such as optical window, solar cells, field effect transistors, light emitting diodes, photocatalysis and biological sensors, optical data storage, optical coding and sensing [6-8].

The physical and chemical properties of the nanocrystalline materials have different properties as compared to their bulk size of the same composition. They show enhanced thickness, hardness, thermal expansion coefficient and magnetic properties [9]. Many methods have been used to deposit thin films so as to control the size, morphology and crystallinity of thin films.Thin films have been obtained by number of growth techniques such as electrodeposition [10], vacuum evaporation [11], pulsed laser deposition [12], successive ionic layer adsorption and reaction (SILAR) method [13] chemical bath deposition [14-15], spray pyrolysis [16], sol-gel and ion implantation techniques [17] and molecular beam epitaxy [18].

In this paper, we have used the Chemical bath deposition (CBD) and the successive ionic layer adsorption and reaction (SILAR) method to deposit the CdS thin films. Both the techniques are simple, reproducible and cost effective as compared to other deposition techniques. The CBD and SILAR techniques has many advantages such as simplicity, no requirement of sophisticated instruments, minimum material wastage, large area deposition and no handling of poisonous gases. Both these methods are slow process which facilitates the better orientation of the crystallites with improved grain structure.

We report the synthesis of CdS thin using CBD [19-21] and SILAR [22-24] techniques at room temperature and deposition of the film on glass substrate. The deposition condition were optimised to get good quality, well adherent films onto glass substrate. The films were characterised for structural, surface morphological, optical, UV-VIS, spectroscopy and electrical properties using the two probe method.

2 Experimental

The CdS thin films were deposited on glass substrate by using CBD and SILAR techniques. Substrate

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cleaning plays an important role in the deposition of thin films. Glass slides were kept in chromic acid for 1 hour and were washed thoroughly with detergent and ultrasonically cleaned. Finally it was rinsed with acetone before use. The starting material used in CBD were Cadmium Sulphate ($CdSO_4$) as Cd^{2+} ion source and thiourea [$CS(NH_2)$] as an S^{2-} ion source. An alkaline solution of ammonia was used to adjust pH of the reaction mixture as a complexing agent. It is added drop by drop in the $CdSO_4$ solution until the initially formed white precipitate is completely dissolved and then 0.5M of $CS(NH_2)$ is poured into the mixture. To vary the composition of the films, different concentration of $CdSO_4$ is used so that the ratio of S/Cd is varied. The films with different thickness were obtained by varying the deposition time period. The glass substrate were immersed in the solution at room temperature and removed after two and half hours. The substrate were then washed with double distilled water. The deposited film yellowish, homogeneous and having good adhesion with the substrate.

The CdS formation is detailed in the following series of chemical reactions :

$$CdSO_4 + NH_4OH \leftrightarrow Cd(OH)_2 + (NH_4)_2SO_4$$

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

$$HN{-}C{-}H_2N \leftrightarrow H\,N{-}C{=}NH_2 \quad N-C$$

Analytical grade cadmium acetate and thiourea were used in the deposition of nanocrystalline cadmium sulphide (CdS) thin films by successive ionic adsorption and reaction technique (SILAR).

Table 1: Optimised preparative parameters for the deposition of CdS thin films by SILAR

Parameters	Precursors solutions	
	Cadmium Acetate	Thiourea
Concentration (M)	0.15	0.15
pH	10.5	10.5
Immersion time (sec)	20	20
Number of SILAR cycles	125	125
Temperature ºC	27	27

The cationic precursor for CdS was 0.15M of cadmium acetate (25ml) then the anionic precursor 0.15M of thiourea (25ml) was taken in separate beakers. For the deposition of CdS thin film, the glass substrate was first dipped in cadmium acetate solution for 20sec, this results in adsorption of Cd^{+2} ions on the surface of the glass substrate and then the substrate was dipped into a solution of 1:1 ratio of ammonia and water for 10sec which acts as a complexing agent to form cadmium ammonia complex. The substrate was again dipped in the anionic precursor S^{2-} for 20sec leading to adsorption and reaction of sulphide ions on the glass substrate. Unreacted sulphide ions were removed by rinsing them. Again the substrate was dipped in double distilled water for 10sec. The procedure was carried out at room temperature. Well adherent and homogenous thin films were formed after repeating 125 cycles.

3. Result and Discussion

3.1 Characterization of CdS thin films

The X-ray diffraction of the thin films were measured on PW-3710 X-ray using diffractometer by using monochromatic CuKα radiation (1.5406ºA) in the range of 2θ from 20-80º. Surface morphology of the samples were carried out on a Scanning Electron Microscope (JEOL JED-2300, JAPAN) with EDAX facility. The optical absorption spectrum of the film was recorded on Spectrophotometer (UV-3600 SHIMADZU, JAPAN) in the wavelength range of 350-850nm. The thickness of the thin films was measured using the Surface Profile Analyser.

3.2 Structural Studies

Fig.1a and fig1b shows a typical XRD pattern of nanocrystalline CdS thin films prepared by CBD and SILAR technique, on glass substrate at optimised preparative parameters. The sharp peaks shows that the deposited films were polycrystalline.

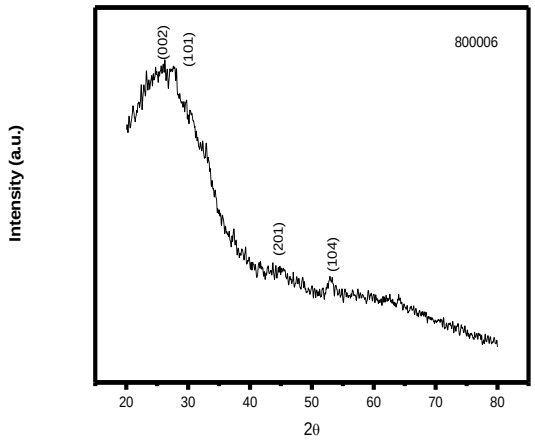

Fig.1a: X-ray diffraction pattern of CdS thin film deposited by CBD

The XRD peak for CdS thin films grown by CBD and SILAR technique revealed cubic (JCPD 800006) and hexagonal (JCPD 800019) crystal structure. For CdS thin film grown by CBD technique, it is seen that the XRD pattern exhibits major peak refection along the (0 0 2), (1 0 2), (1 0 2), (2 0 1) and (1 0 4) planes. For the films deposited by SILAR techniques substantial change in the peak intensity and position is observed. Major peak intensity is observed along the (1 1 1), (2 0 0), (2 2 0) and

(3 1 1) planes. The average crystallite size of the material was calculated by the Scherrer's relation [18]

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where λ = 1.5406 Aº for CuKα, β is the full width at half maximum (FWHM) of the peak and θ is the diffraction/Bragg's angle. The average crystallite size of the as deposited CdS thin film is 6.97nm for CBD technique and 5.56nm for SILAR technique at optimized preparative parameters. It is observed that the crystal size obtained by SILAR method is smaller as compared to CBD method.

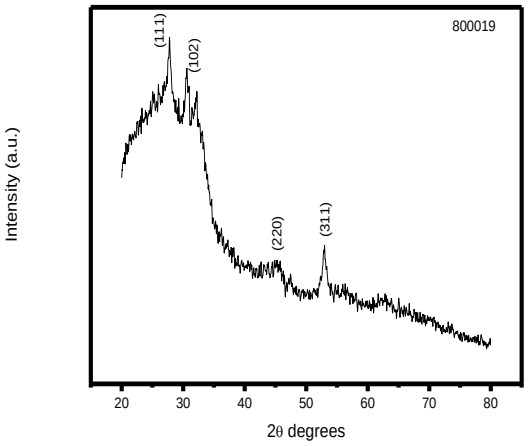

Fig.1b: X-ray diffraction pattern of CdS thin film deposited by SILAR

3.3 Morphological Studies

The scanning electron micrographs of the nanocrystalline CdS thin films, prepared by CBD and SILAR technique, of thickness 1145nm and 1694.nm respectively as shown in Fig.2a and Fig.2b respectively. SEM micrographs shows that the film is well adherent, homogenous and well covered to the substrate without any cracks or pinholes in both the cases. The EDAX technique is used to find out the quantitative composition of CdS film deposited on the glass substrate. The EDAX was recorded in the energy region 0-20KeV as shown in Fig.3a and Fig.3b respectively.

The presence of EDAX peaks for Cd and S at 3.2eV and 2.3eV respectively for CBD and SILAR are conformed from analysis. The atomic percentage of cadmium is more than that of sulphur in both techniques hence the thin film of CdS is rich in cation. Thus it is an n-type material which can be used as an window layer in photovoltaic cells.

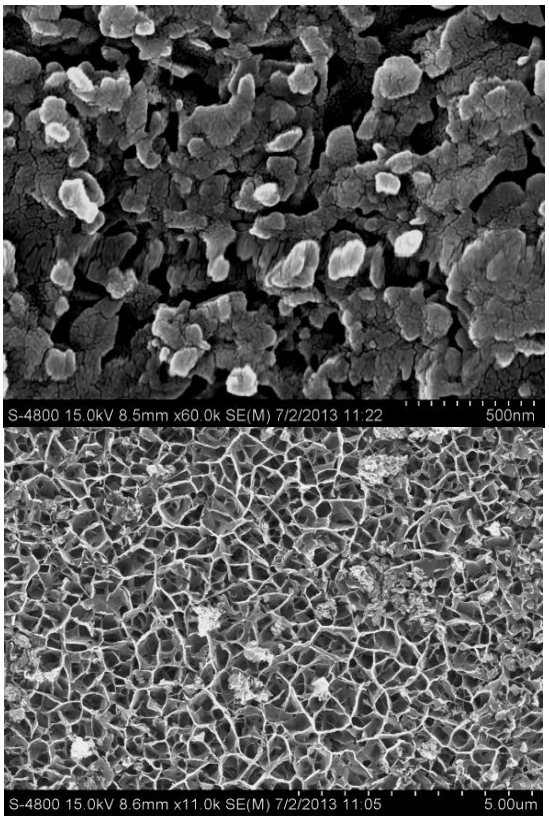

Fig.2a and **Fig.2b** SEM micrograph of CdS thin films deposited by CBD and SILAR

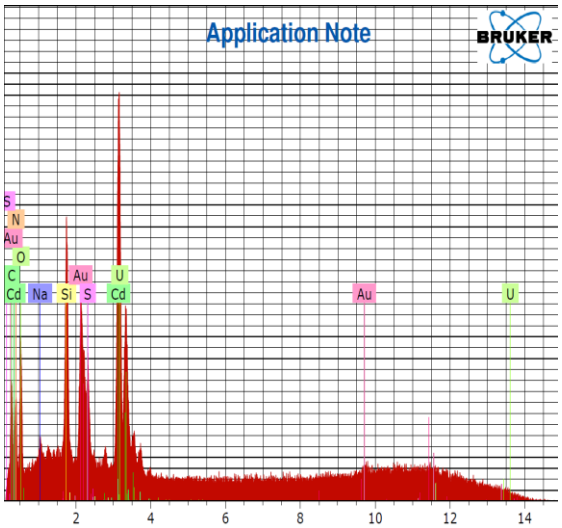

Fig.3a: EDAX micrograph of CdS thin films deposited by CBD.

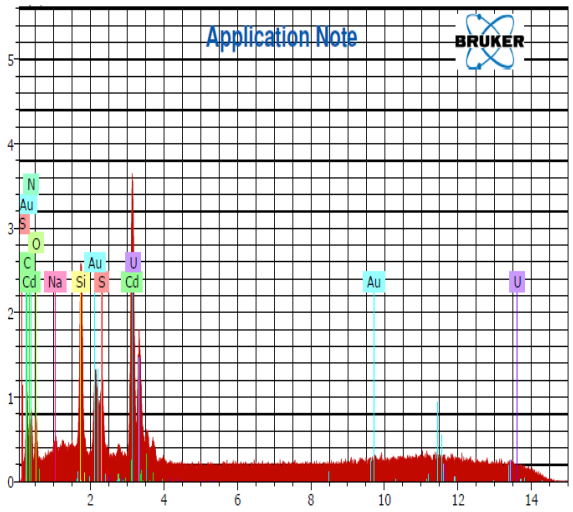

Fig.3b: EDAX micrograph of CdS thin films deposited by SILAR.

3.4 Optical studies

The absorption spectrum of the CdS film has been recorded at room temperature without considering losses due to reflection and transmission. Fig.4a and Fig.4b shows a plot of absorption coefficient versus wavelength for nanocrystalline CdS thin films prepared by CBD and SILAR technique respectively. The absorption coefficient is of the order of

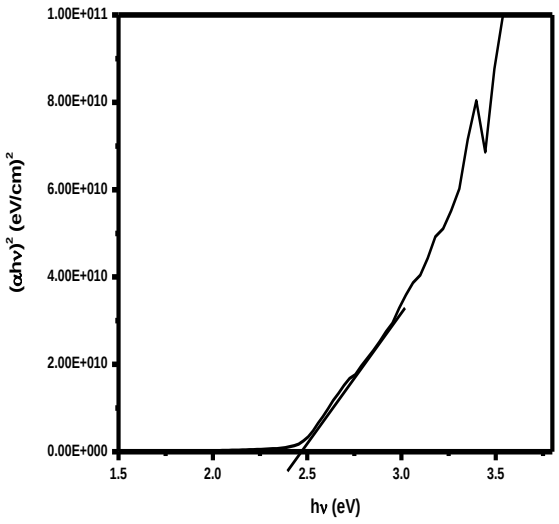

Fig. 4a: Variation of $\alpha h\upsilon^2$ with photon energy ($h\upsilon$) for CdS thin film deposited by CBD technique.

The band gap was obtained using the following equation coefficient for a semiconductor [25]

$$\alpha = \frac{A(h\gamma - E_g\ )^n}{h\gamma}$$

Where A is a constant, α the absorption coefficient and n is equal to ½ for direct band gap semiconductors. The energy intercept of a plot $(\alpha h\gamma)^2$ versus $h\gamma$ (Fig.4a and Fig.4b) gives E_g for direct transition. The plot shows that the energy gap is of the order of 2.48eV and 2.54eV for CBD and SILAR grown for CdS thin films, which agrees well the standard value reported for CdS by Kaintla. The greater band gap of cadmium sulphide deposited by SILAR technique, might be due to the small crystalline size as compared to that of the crystalline size from chemical bath deposition technique.

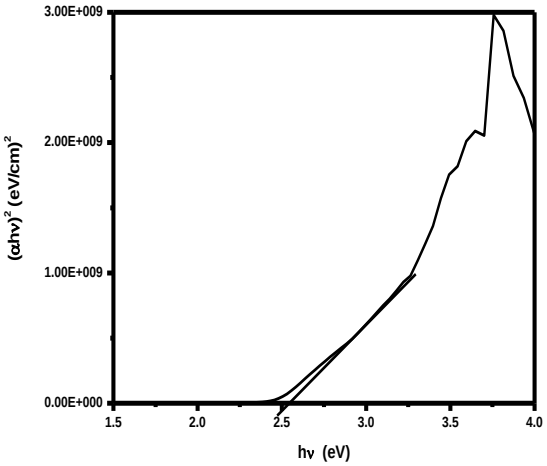

Fig. 4b: Variation of $(\alpha h\upsilon)^2$ with photon energy ($h\upsilon$) for CdS thin film deposited by SILAR technique.

3.5 Electrical properties

For electrical characterization, ohmic contacts to the films were made with silver paste. Ohmic character of the contact was verified by I-V measurements. Resistivity of CdS thin films is about 6.414 x 10^5 Ω-cm and 7.42 x 10^5 Ω-cm for CBD and SILAR techniques respectively. The resistance of hexagonal CdS phase obtained by CBD is lower than that of the cubic phase obtained by SILAR technique.

4 Conclusion

In this paper, we have reported the preparation of nanocrystalline thin films using the chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) techniques at room temperature. The XRD studies of cadmium sulphide thin films deposited by CBD and SILAR technique have cubic and hexagonal structure with particle size of order of 6.97nm and 5.56nm respectively. The optical band gap of the film deposited by CBD and SILAR is found to be 2.4eV and 2.54eV. The resistivity of CdS film deposited by CBD was found to have lower value as compared to resistivity obtained by SILAR technique.

Acknowledgement:

The authors express thanks to the Head of Department, Physics, North Maharastra University, for providing the characterization facilities.

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