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Room Temperature Deposition of Nanocrystalline CdS Thin Film by Successive Ionic Layer Adsorption and Reaction (SILAR) Method

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Abstract

Cadmium Sulphide (CdS) thin films are deposited on glass substrate by relatively simple, quick and cost effective successive ionic layer adsorption and reaction (SILAR) method at room temperature (27^{0}C). For fine nanocrystalline thin film growth the parameters including concentrations of cationic and ionic precursors, number of immersion cycle, immersion time and pH of the solution are optimized. A further study has been made for structural, surface morphological and optical properties of the film using X-ray diffraction (XRD), EDAX, scanning electron microscopy (SEM), Atomic force electron microscopy (AFM) and optical absorption method. The as deposited CdS nanocrystlline film exhibited hexagonal phase with optical band gap (Eg) of 2.20eV and electrical resistivity 10^6 Ω-cm. SEM and AFM images confirmed that films of smooth surface morphology and nanocrystalline nature with fine crystallites 40 nm diameter respectively.

Keywords: Nanocrystalline thin films, cadmium sulphide, Band gap, X-ray diffraction, morphological and optical properties.

Introduction

Nanocrystalline cadmium sulphide (CdS) is wide band gap material belongs to II-VI group compound materials. Its band gap varies between 2.1 to 2.4 eV, depending upon composition. The CdS thin films have been used in applications such as optical window solar cells[1,2] field effect transistors, light emitting diodes[3,4], photocatalysis and biological sensors[5,6] optical coding, optical data storage and sensing[7], nonlinear integregated optical device[8]. In recent years there has been growing interest in developing techniques for preparing semiconductor nanoparticles and thin films because the properties in nano form differ significantly from those of their bulk counter parts. Therefore there is much interest in physical properties of nanometer size (20-80nm) semiconductor materials due to their novelties; their properties are different and often superior to those coarse grained polycrystalline materials and also amorphous alloys of same composition[9,10]. In addition to increased strength, hardness, enhanced diffusivity, improved quality, roughness, reduced elastic modulus, higher thermal exapansion coefficient, lower thermal conductivity and superior soft magnetic properties[11]. Much effort has been made to control the size, morphology and crystallinity of CdS thin film. In past many researchers have been deposited CdS thin films by both gas phase and liquid phase methods. Gas phase deposition method includes vacuum evaporation[12], flash evaporation, activated reactive evaporation (ARE), sputtering and chemical vapor deposition (CVD)[13] whereas liquid phase include electrodeposition[14], chemical bath deposition (CBD)[15-17] and spray pyrolysis methods. Among them, chemical bath deposition (CBD) is well known as a low temperature aqueous technique for depositing large area of semiconductor thin films. Many researchers have deposited CdS thin film by CBD. In CBD method the precipitation and film deposition takes place when ionic product exceed the solubility product which produce wasteful unavoidable and uncontrollable bulk precipitate[18]. To overcome the difficulty, we have used the SILAR method for the formation of CdS thin film. Successive ionic layer adsorption and reaction (SILAR)[19,20] is simple, less expensive and useful for large area deposition of any composition, easily controlled film thickness method at atomic level. This method does require sophisticated instruments and conductive substrate. The SILAR method is suitable for growing thin multilayer structure due to low temperature since diffusion of ion is slow. The growth of the film can be easily controlled through various parameters including concentration of bath temperature, immersions time and immersion cycles, etc.

In this paper, we report SILAR method for the synthesis of nanocrystlline CdS thin film on the glass substrate. The deposition condition for CdS thin films were optimized to get good quality, well adherent films onto glass substrate. The as deposited fils were characterized for structural, surface morphological, optical, uv-vis. spectroscopy, and electrical dc. two probe method technique.

Material and Methods

Deposition of nanocrystalline thin film: All Loba analytical grade (AR) cadmium sulphate, thiourea and liquor ammonia were used for deposition of CdS thin film. In the synthesis of CdS thin film the cationic precursor was 0.1M cadmium

sulphate solution complexed with ammonia solution at pH=10 for cadmium ion and anionic precursor was 0.1M thiourea solution for sulphide ion. Direct exchange of cationic and anionic ions were modified by means of rinsing in double distilled water. Each SILAR cycle consist of i) adsorption of Cd^{2+} ions from cadmium sulphate solution for 20s, ii) rinsing with double distilled water for 10s, iii) reaction with sulphide precursor solution from thiourea solution for 20s and finally iv) rinsing with double distilled water for 10 s. This process was repeated for 40 times to get desired film thickness.

Substrate cleaning : The deposition was carried out by using Corning glass slides (25mm X75mm X 1.35mm) as substrate which were initially boiled in concentrated chromic acid for 30 min. rinsed in acetone, deionsed water and finally ultrasonically cleaned.

Characterization of thin film: The thickness of the thin films was measured by sensitive gravimetric weight difference method. The structural characterization of the films was carried out using Philips (PW-3710) X-ray diffractometer with CuKα radiation (α = 1.5404°A) in 2θ range from 20^0-80^0. The surface morphological study of CdS films was carried out by scanning electron microscopy using a Model JOEL, JSM 6360A and Energy dispersive X-ray analysis (E-DAX) were recorded on Energy dispersive X-ray spectrometer attached to the SEM model. Three dimensional surface morphology of the thin film was recorded using atomic force microscopy by Quesant Instrument Corporation, Q-Scope 250. The optical absorption spectrum of the film was recorded on Systronic spectrophotometer in the wavelength range of 350-850 nm. For the electrical resistivity.

Results and Discussion

The film formation mechanism: The film formation of CdS thin films by SILAR method is as shown in figure 1.

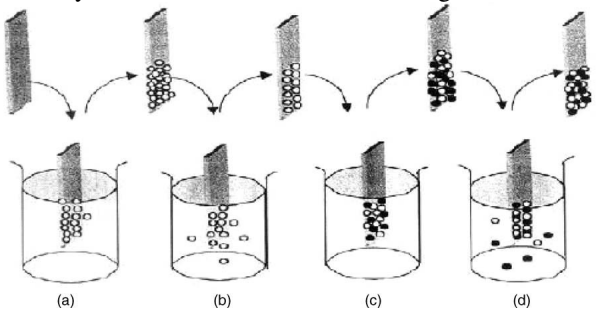


Figure- 1
The scheme of SILAR trend for the deposition of CdS thin films

To deposit nanocrystlline CdS thin film one SILAR cycle involves the following four steps: i. Adsorption of Cd^{2+} , a well cleaned glass substrate is immersed in the 0.1M Cadmium sulphate solution having Cd^{2+} cadmium ions are adsorbed on glass substrate. ii. Rinsing the unabsorbed Cd^{2+} ions are separated out by dipping the substrate in double distilled water. iii. Reaction with S^{2-}, sulphide ions were adsorbed from an aqueous solution of 0.1 M thiourea. iv. Rinsing finally the substrate was washed with distilled water, thus one SILAR cycle is completed. After few number of such SILAR cycles, CdS thin film is formed onto glass substrate.

The film formation reaction mechanism can be written as

$$Cd^{2+} + SO_4^{2-} + CH_2N_2 + S^{2-} \longrightarrow CdS + CH_2N_2 + SO_4^{2-}$$

Repeating number of SILAR cycle for different concentrations, immersion cycle and immersion times, preparative parameters for best quality CdS thin films were optimized as illustrated in table 1.

Table-1
Optimized preparative parameters for CdS thin films

Parameters	Precursors solutions	
	Cadmium sulphate	Thiourea
Concentration (M)	0.1	0.1
pH	~ 10	~10
Immersion time (S)	20	20
Rinsing time (S)	10	10
Number of SILAR cycle	40	40
Temperature(K)	300	300

The variation of film thickness against concentration of cadmium sulphate for 40 immersion cycle is as shown in figure 2.

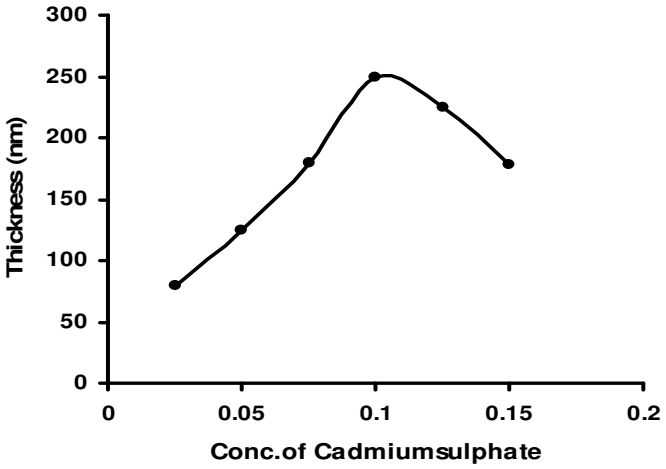


Figure-2(a)
The Variation of CdS film thickness as function of concentration of Cadmium sulphate for fixed concentration of thiourea

The CdS film formation was started at concentration of 0.025M of cadmium sulphate but it is optimize for maximum thickness at 0.1M concentration. After this CdS film thickness was decreased due to formation of outer porous layer and peeling off from glass substrate. The thickness of CdS thin film was measured by weight difference method. Figure 2(a) and figure 2 (b) shows the variation of film thickness with deposition time and no of deposition cycles.

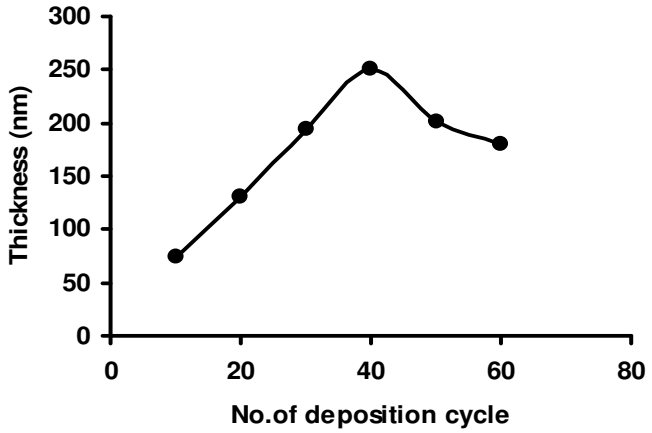


Figure-2(b)
Variation of CdS film thickness as a function of number of deposition cycles at constant concentration of Cadmium Sulphate (0.1 M) and concentration of thourea (0.1 M)

Initially film thickness increases with deposition time. This CdS film had maximum terminal thickness of 250 nm for 40 immersion cycle, after this film thickness starts to decrease due to peeling of the material from the substrate.

Structural studies : Figure 3 shows typical XRD diffraction pattern of nanocrystalline CdS thin film onto glass substrate recorded on Model Bruker D8 advance AXS X-ray diffractometer with scanning angles in the range 20 ⁻ 80 degree using CuK_{α} radiation (λ=1.5406 Å).

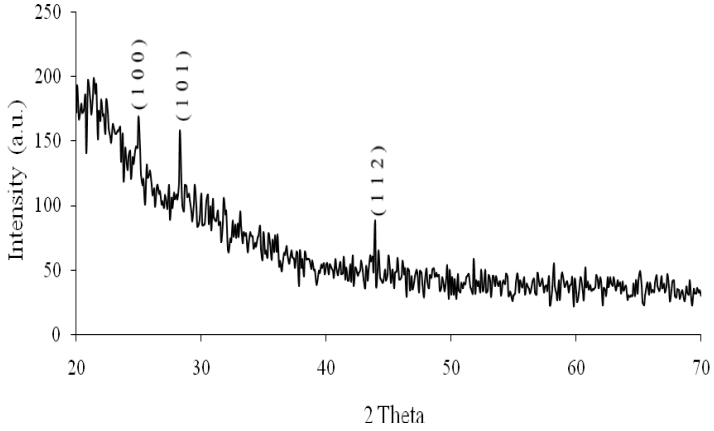


Figure-3
XRD pattern of CdS thin film deposited by SILAR method onto glass substrate

The XRD peak reveals that CdS has nanocrystalline with hexagonal crystal structure. The average crystallite size was calculated by the Scherrer reletion

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

where, λ=1.5406 Å 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 as-deposited CdS thin film is 40 nm. at optimized preparative parameters.

Surface morphological studies: The scanning electron microscopy technique is familiar for the study of surface morphology of metal chacogenides in the thin film form. The parameter optimized thin film of CdS is used for SEM analysis. Figure 4 shows the SEM micrograph of CdS thin film. The film is homogeneous, well adherent and covers glass substrate without cracks and pin hole. It was observed that the film was uniform yellowish and well substrate covered with homogeneous fibrous structure[21]. The E-DAX technique is used to determine quantitative composition of CdS films deposited on glass substrate. The EDAX was recorded in the energy region 0-20 keV. The presence of EDAX peaks for Cd and S are conformed from analysis. The composition ratio was 1:1 of atomic mass percent for Cd and S respectively as shown in figure 5. From the compositional analysis we found that deposited cadmium and sulphur are equal in proportion.

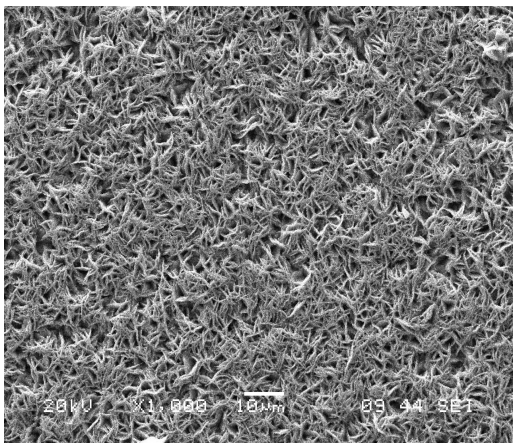


Figure-4
The SEM micrograph of as-deposited CdS film on glass substrate at room temperature

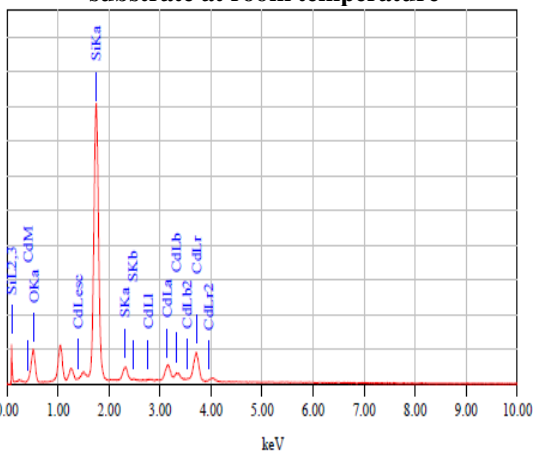
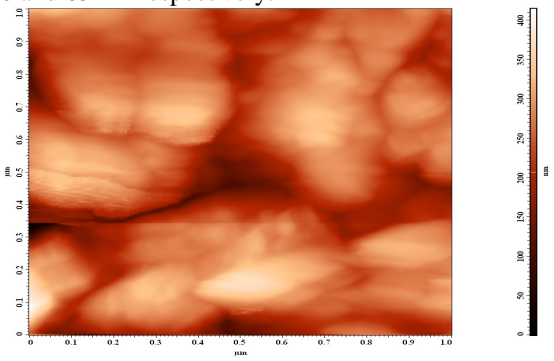


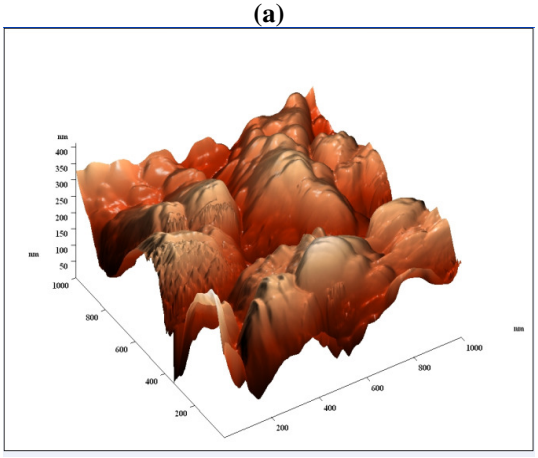
Figure-5
The EDAX analysis of as- deposited CdS on glass substrate at room temperature

AFM Studies: Figure 6 (a) and figure 6 (b) show the three-dimensional and two-dimensional atomic force microscopy (AFM) images for CdS thin films deposited on glass substrate respectively. All the AFM images were measured for an area of

1000 nm x 1000 nm. The atomic force microscopy images of the films prepared on glass substrate for 40 immersion cycle these clusters are homogeneously distributed over the whole surface. The substrate surface is well covered with grains that are uniformly distributed over the surface. The average sizes of smaller grains are observed to be 90 nm. The surface is relatively uniform. The average surface roughness and thickness is 48.30 and 65 nm respectively.



(a)



(b)

Figure 6
(a) and (b), the 3D and 2D atomic force microscopy (AFM) images for CdS thin films respectively

Optical properties: The optical properties of as deposited CdS thin films was studied at room temperature using UV-spectrometere in the wavelength range 450-800 nm. showing film is highly absorptive.

Figure 7 shows the absorbance spectra of as deposited CdS thin films. Absorbance coefficient α associated the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using relation[22,23] ,

$$\alpha = 2.3026\ A/t \quad (2)$$

The absorption coefficient α was analyzed using the following expression for near age optical absorption of semiconductors

$$(\alpha h\upsilon) = K\ (h\upsilon - E_g)^{n/2} \quad (3)$$

Where k is Boltzmann's constant, E_g is separation between valance and conduction bands and n is constant that is equal to 1 for direct band gap semiconductor.

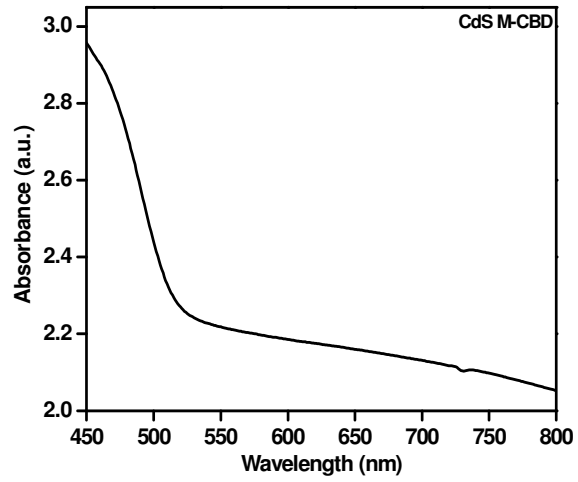


Figure-7
Absorbance spectra of as-deposited CdS thin films for different thicknesses on glass substrate at room temperature

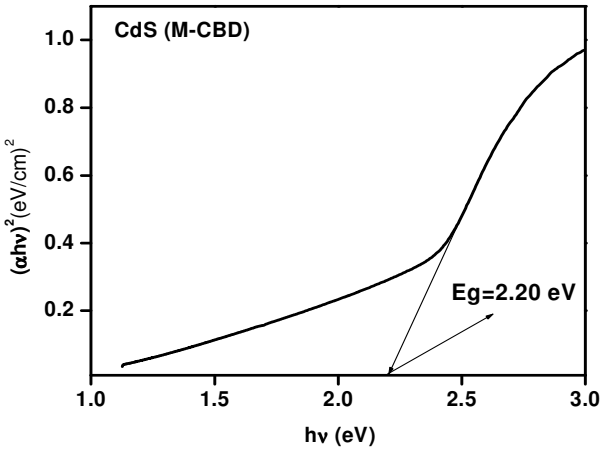


Figure-8
Plot of (αhυ) versus hυ of as-deposited CdS thin films

Figure 8 shows a plot of (αhυ) versus hυ which is linear at the absorption edge showing direct band gap material. The band gap were determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus hυ plot is extrapolated to α = 0. The observed band gap value of CdS film was estimated to be 2.20 eV. Agrees well with reported value for CdS[24,25]. The electrical resistivity was found to be of the order of 10^6 Ω-cm.

Conclusion

In this paper we have reported SILAR method for the preparations of nanocrystalline CdS thin film on glass substrate. Structural analysis reveals that the deposited films were

polycrystalline nature showed hexagonal structure of CdS thin films. The average crystallite size is 40 nm. The SEM and AFM micrograph reveals that substrate is homogeneous, well adherent and covers glass substrate without cracks and pin hole and average grain size is 90 nm. The optical band gap of CdS thin film was found to be 2.20 eV.The electrical resistivity at room temperature of CdS thin film was found to be 10^6 Ω-cm .

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