Structural, optical and electrical properties of nanocrystalline cadmium sulphide thin films deposited by novel chemical route

U M Jadhav[1], M S Shinde[1], S N Patel[2] & R S Patil[1]*

[1]P S G V P M'S Arts, Science & Commerce College Shahada, Dist, Nandurbar 425 409

[2]S P D M Arts, Commerce and Science College, Shirpur,India

*E-mail: rspatil_shahada@yahoo.co.in

Nanocrystalline semiconducting cadmium sulphide(CdS) thin films have been deposited on glass substrate by relatively simple, quick and cost effective chemical bath route. The deposition kinetics played important role to get good quality nanocrystalline films with uniform thickness. Hence, the preparative parameters such as concentration, temperature, deposition time, pH of solution have been optimized. The characterization of as deposited thin films was carried out for the structural, compositional, surface morphological, optical and electrical properties using X-ray diffraction (XRD), EDAX, Scanning electron microscopy (SEM), UV-VIS Spectra and *dc* two point probe method.

Keywords: Nanocrystalline thin films, Cadmium sulphide, Band gap

1 Introduction

Nanocrystalline cadmium sulphide (CdS) belongs to II-VI group compound of semiconducting material. Its band gap varies between 2.1 to 2.45 eV. The CdS thin films have wide range of well perspective applications such as field effect transistors, light emitting diodes, photocatalysis and biological sensors[1,2] optical coding, optical data storage and sensing[3,4], nonlinear integregated optical device[5]. 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[6,7]. Therefore, much effort has been made to control the size, morphology and crystallinity of CdS thin film. For the deposition of CdS thin films both gas phase and liquid phase methods have been used. Gas phase deposition method includes vacuum evaporation, flash evaporation, activated reactive evaporation (ARE), sputtering and chemical vapour deposition(CVD) whereas liquid phase include electrodeposition[8], successive ionic layer adsorption and reaction[9,10] (SILAR), chemical bath deposition[11-13] (CBD) and spray pyrolysis methods[14]. Among them, chemical bath deposition (CBD) is well known as a low temperature aqueous technique for depositing large area of semiconductor thin films. It is very simple, cost effective and also capable in growing nanocrystals, microcrystal and epitaxial structure under various growth condition.

In the present investigation, CdS thin films have been deposited using chemical bath deposition method in alkaline bath. The structural, compositional, surface morphological and optical properties of the as deposited CdS thin films have been studied.

2 Experimental Details

2.1 Substrate cleaning and CdS film growth

The deposition was carried out by using corning glass slides (25 mm × 75 mm × 1 mm) as substrate which were initially boiled in concentrated chromic acid for 30 min rinsed in acetone, deionised water and finally ultrasonically cleaned. All analytical grade (AR) reagents were used as it is without further purification for the deposition of CdS thin films. Aqueous solution of 0.1 M cadmium sulphate, 0.1 M thiourea and complexing agent liquor ammonia was used. Initially 20 ml of $CdSO_4$ solution and 2.5 ml ammonia was placed in 50 ml beaker, after stirring for several minutes solution becomes homogeneous under continuous stirring, 20 ml thiourea solution was introduced then cleaned glass substrate was vertically immersed into the prepared bath at room temperature.

2.2 Characterization of thin film

The thickness of the thin films was measured by a surfcom 480Å profilometer. The structural characterization of the films was carried out using Philips (PW-3710) X-ray diffractometer with CuKα
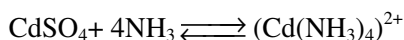
radiation (α = 1.5404Å) in 2θ range 20°-80°. The surface morphological study of CdS films was carried out by scanning electron microscopy using a Model JOEL, JSM 6360A and Energy dispersive X-ray analysis (E-DAX) were recorded on Energy dispersive X-ray spectrometer attached to the SEM model. Three dimensional 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 350-850 nm.
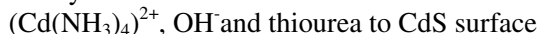
3 Results and Discussion

3.1. Film formation mechanism

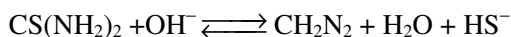The film formation reaction mechanism[16,17] for CdS thin film is:
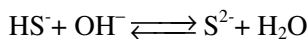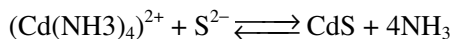
i.   Formation of a complex

$$CdSO_4 + 4NH_3 \rightleftharpoons (Cd(NH_3)_4)^{2+}$$

ii. Catalytic diffusion of ions
$(Cd(NH_3)_4)^{2+}$, OH^- and thiourea to CdS surface

iii. Thiourea dissociates in a alkaline medium as

$$CS(NH_2)_2 + OH^- \rightleftharpoons CH_2N_2 + H_2O + HS^-$$

iv. Formation of sulphide ion

$$HS^- + OH^- \rightleftharpoons S^{2-} + H_2O$$

v.   Formation of CdS film

$$(Cd(NH3)_4)^{2+} + S^{2-} \rightleftharpoons CdS + 4NH_3$$

Making several trials for different concentrations, *p*H of the solution, deposition time, preparative parameters were optimized for best quality CdS film. The variation of film thickness with concentration of cadmium sulphate, keeping concentration of thiourea 0.1 M is as shown in Fig. 1.

The CdS film formation started at concentration of 0.025 M of cadmium sulphate but it was optimized 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[15]. The thickness of CdS thin film was measured by Profilometer. Fig. 2 shows the variation of film thickness with deposition time.

Initially film thickness increases with deposition time. This CdS film had maximum terminal thickness of 250 nm for deposition time of 2 h after this film thickness starts to decrease due to peeling of the material from the substrate[15].
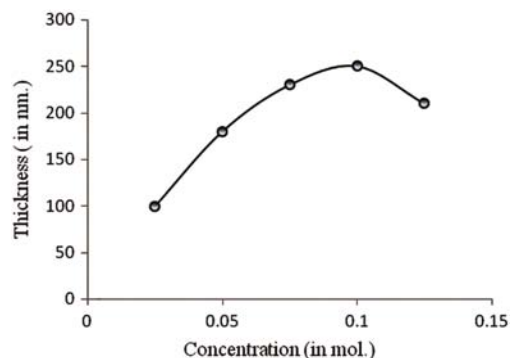

Fig. 1 — Variation of CdS film thickness as a function of concentration of cadmium sulphate for fixed concentration of thiourea
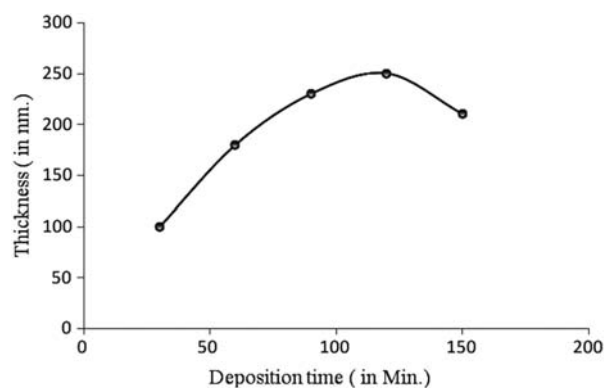

Fig. 2 — Variation of as deposited CdS film thickness as a function of deposition time

3.2 Structural studies

X-ray diffraction patterns of the film were recorded on Model Bruker D8 advance AXS X-ray diffractometer with scanning angles in the range 20-80 degree using CuK$_\alpha$ radiation (λ=1.5406Å).

Figure 3 shows X-ray diffraction pattern of as-deposited CdS thin film on glass substrate by chemical bath deposition method. In the present diffraction pattern of XRD, four dominant peaks at 26.5°, 30.7°, 44.0° and 52.1° corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of CdS are seen with cubic crystal structure[14]. An average value of the crystallite size at the (2 0 0) plane can be obtained by applying the Debye-Scherrer's equation:

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

where, λ=1.5406Å for CuKα, β is the full width at half maximum (FWHM) of the peak and θ is the diffraction/Bragg's angle. The sample as-deposited CdS resulted in an average crystallite size of approximately 40 nm.
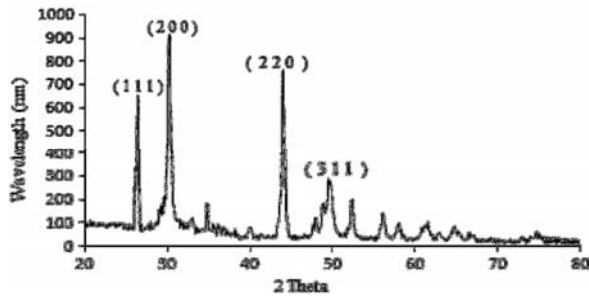
Fig. 3 — X-ray diffraction pattern of as-deposited CdS thin films For different thicknesses on glass substrate at room temperature
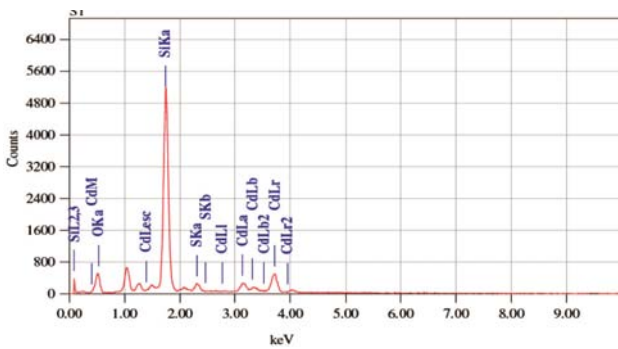

Fig. 4 — Energy dispersive X-ray analysis of as-deposited CdS film on glass substrate at room temperature

Fig. 5 — Surface morphology of as-deposited Cu_2S on glass substrate at room temperature by scanning electron microscopy studies

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

The E-DAX technique is used to determine quantitative composition of CdS films deposited on glass substrate. The composition ratio was 1:1 of atomic mass per cent for Cd and S, respectively as shown in Fig. 4. From the compositional analysis, we found that deposited cadmium and sulphur are equal in proportion.

3.3 Surface morphological studies

Scanning electron microscopy (SEM) is a versatile technique for studying microstructure of thin films. The CdS thin film with 250 nm thickness was used to study the surface morphology using a scanning electron microscopy.

Figure 5 shows a scanning electron microscope of CdS thin film at X 10000 magnification the scale bar length is 1µm the average grain size of CdS thin films was estimated using Cotrells methods[18]. The as-deposited film shows net like nanostructure with symmetry in shape. The film surface looks smooth and uniform. It was observed that the film was uniform yellowish and well substrate covered.

Figure 6 (a and b) shows 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
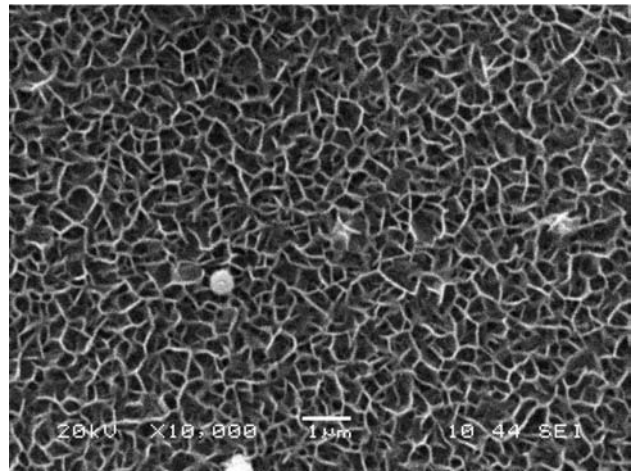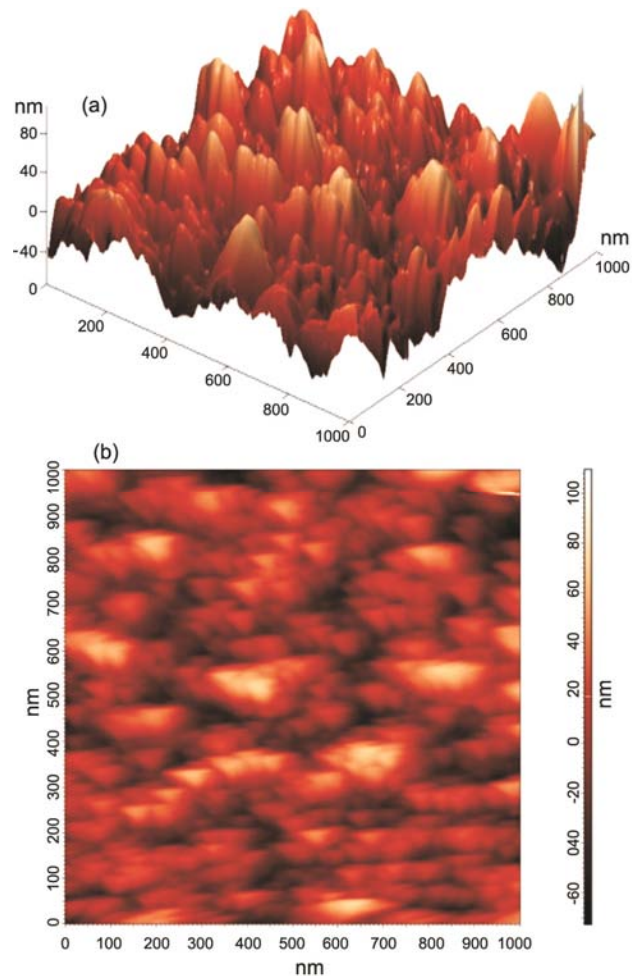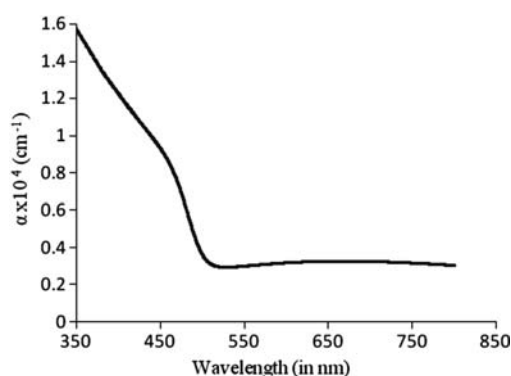
Fig. 7 — Absorbance spectra of as-deposited CdS thin films for different thicknesses on glass substrate at room temperature

measured for an area of 1000 nm×1000 nm. The atomic force microscopy images of the films prepared on glass substrate indicate spherical shaped grains. 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 40 nm. The surface is relatively uniform. The average surface roughness and thickness is 48.30 and 65 nm, respectively.

3.4 Optical properties

The optical properties of CdS thin films are determined from absorbance measurement in the range 350-900 nm.

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

$$\alpha = 2.3026\, A/t \qquad \qquad \dots (2)$$

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

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

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. The band gap was determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus $h\upsilon$ graph as shown in Fig. 8.

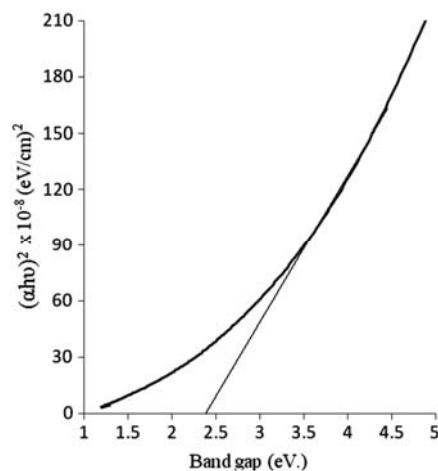The observed band gap value of the films was 2.4 eV. This is found to be in good agreement with the reported values[19].

Fig. 8 — Variation of $(\alpha h\upsilon)^2$ verses $h\upsilon$ of as-deposited CdS thin film on glass substrate at room temperature
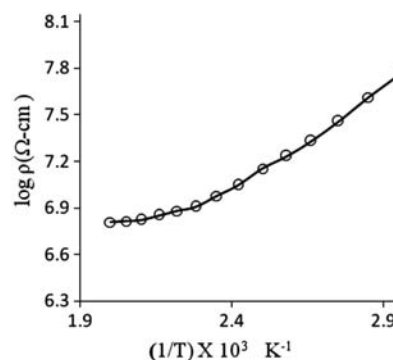

Fig. 9 — Variation of $(\log \rho)$ with $(1000/T)$ for as-deposited CdS thin film on glass substrate

3.5 Electrical resistivity

The electrical resistivity of ZnS thin films was measured using *dc* two point probe method.

Figure 9 shows the variation of log of resistivity $(\log \rho)$ with reciprocal of $1/T \times 10^3 K$ for all films. The resistivity follows the relation:

$$\rho = \rho_0 \exp(E_a/kT) \qquad \dots(4)$$

where ρ is resistivity at temperature T, ρ_0 is a constant, k is Boltzmann constant, E_a is activation energy for conduction. From Fig. 9, resistivity of CdS sample decreases with temperature indicating semiconducting nature of thin film. The electrical resistivity at room temperature of the CdS thin film onto the glass substrate was found about 6.463×10^7 Ω-cm.

4 Conclusions

A simple chemical bath deposition method was used for preparation of nanocrystalline CdS thin films on glass substrate. The XRD and EDAX study showed the cubic structure of CdS thin films. The SEM micrograph reveals that substrate is well covered and average grain size is 40nm. The optical bandgap was found to be 2.4 eV. The electrical resistivity at room temperature of the CdS thin film onto the glass substrate was found to be about $6.463 \times 10^7 \, \Omega$-cm.

Acknowledgement

References

1 Alivisators A P, *Science,* 271 (1996) 933.
2 Klevin D I, Roth R, Lim A K I & Alivisators A P, *Nature,* 389 (1997) 699.
3 Sarma K C, bordolo R K, Sarma M & Gangurly J N, *J Instrum Soc India,* 31 (2001) 216.
4 Cao G, *Imperical college Press,* 349 (2004).
5 Senthil K, Magalraj D & Narayandas S K, *Appl Surf Sci*, 169.
6 Henglein A, *Chem Rev*, 89 (1989) 1861.
7 Fukuka A, Sakamoto Y, Guan S, Ingaki S, Sugimoto N, Fukushima Y, Hirahara K, Lijima S & KIkawa M, *J Amer Chem Soc*, 123 (2001) 3373.
8 Basol B M, Tseng E S & D S Lo*, US Patent*, 548 (1985) 681.
9 Nicolaue Y F & M Dupuy, *J Elctrochem Soc*, 137 (1990) 2915.
10 Nicolaue Y F, *Appl Surf Sci*, 22 (1985) 1061.
11 Kale S S, Jadhav U S & Lokhande C D, *Indian J Pure & Appl Phys*, 34 (1996) 324.
12 Mondal A, Chaudhary T K & Pramanik P, *Sol Energy Matter* 7 (1983) 431.
13 Kaladargh Yashar Azizian, Murador M B & Ali Kaodayari, *J Cryst Growth*, 175 (2007) 305.
14 Chamberlin R R, *J Electrochem Soc*, 113 (1966).
15 Shinde M S, Ahirrao P B, Patil I J & Patil R S, *Indian J Pure & Appl Phys*, 49 (2011) 765.
16 Pavaskar N R,Menezes C A & Sinha APB, *J Elctrochem Soc*, 124 (1977) 743.
17 S Chandra, Pandey R K & Agrawal R C, *J Phys D Appl Phys*, 13 (1980) 1757.
18 A Cottrell, *Intorduction to Mettallurgy*, Arnold, Londan, (1975) 173.
19 Kathirvel D, Suriyanarayananb N, Prabahar S, Srikanth S & Rajasekaran P, *Chalcogenide Lett*, 8 (2010) 32.