

Deposition of Cadmium Sulphide Thin Films by Photochemical Deposition and Characterization

H.L. Pushpalatha, R. Ganesha*

Department of Physics, Yuvaraja's College, University of Mysore, Mysore-05, India

(Received 02 December 2014; published online 25 March 2015)

Deposition of cadmium sulphide (CdS) thin films on glass substrates in acidic medium by photochemical deposition (PCD) and studies by several characterizations are presented. The structural characterization of the thin films was carried out by XRD. The elemental composition of the thin films was carried out by EDAX. The optical properties have been studied in the wavelength range 200-900 nm and the optical transition has been found to be direct and allowed. The morphological properties are studied by AFM and electrical properties are studied by four probe technique.

Keywords: Thin films, II-VI semiconductors, UV-photons, Photochemical deposition, XRD, EDAX, AFM, Four-point probe technique.

PACS numbers: 73.90. + f, 73.61.Ga,
61.05.Cp, 68.37.Ps

1. INTRODUCTION

CdS is a II-VI metal chalcogenide compound semiconductor with a direct band gap (2.42 eV) finds application in the field of optoelectronic devices [1], multi-layer LED, optical filters [2], photoconductor [3], thin film FET [4], gas sensors [5] and in thin film solar cells [6] in the last few decades. Deposition of thin films occurs by various methods. Among them, electrochemical deposition (ECD) [7, 8] and chemical bath deposition (CBD) [9-11] occurs in aqueous medium. In ECD, deposition occurs in the presence of external electric field while CBD is an electroless-deposition method overcoming the necessity of a conducting substrate. But controllability of the chemical reaction and deposition process is poor in CBD. A novel PCD technique providing better controllability has been developed in 1997 by Masaya Ichimura, Goto and Arai [12]. In PCD, a substrate held in an aqueous solution containing $S_2O_3^{2-}$ and Cd^{2+} ions is irradiated with UV light. The PCD-CdS film is deposited only in the irradiated region of the substrate, not in the whole of the solution unlike in CBD and hence offers better controllability. The thio-sulfate ions absorb the UV photons and release solvated electrons and sulphur atoms, which react with Cd^{2+} to form CdS. The rate of deposition is proportional to the intensity of UV radiation.

2. EXPERIMENT

CdS thin films were deposited on soda lime glass substrates of dimension ($2.5 \times 2.5 \times 0.145 \text{ cm}^3$). The substrates were ultrasonically cleaned using acetone, dried in an oven to ensure good adherence and uniformity of the film. A schematic diagram of PCD is as shown in Fig. 1. Aqueous solution of 75 mL of 0.2 M cadmium sulfate ($CdSO_4$) as cadmium source and 50 mL of 0.2 M sodium thiosulfate ($Na_2S_2O_3$) as sulphur source constitutes 125 mL of growth-solution in a glass beaker containing magnetic peddle (length 14 mm). The diameter of the glass beaker was about

5.5 cm. After stirring the solution for few seconds, dilute sulphuric acid (H_2SO_4) was added drop wise to reduce pH of the solution to 3.6. Then the beaker was kept on a heater cum magnetic stirrer (Remi). The cleaned substrate was held horizontal in the aqueous solution at a distance of 3 mm from the solution-surface. Stirring rate was adjusted to 300 rpm. The deposition was at room-temperature ($28^\circ C$).

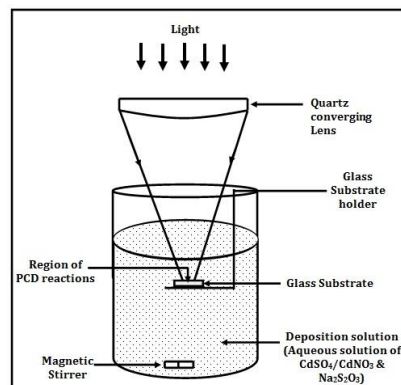


Fig. 1 – Schematic PCD-apparatus

The substrate was illuminated by light from a high pressure mercury arc lamp 500 W using a spherical quartz lens (Fig. 2). The solution was being continuously stirred to promote transport of the ions to the illuminated region (10 mm). After 1 hour of deposition, the substrate was removed and dried in an electric oven. CdS thin film was found deposited only on the illuminated region of the substrate.

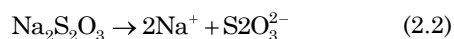
2.1 Photochemical Reaction

$CdSO_4$ dissociates into Cd^{2+} and SO_4^{2-} in an aqueous solution by the following reaction:



* rajeshganesha@gmail.com

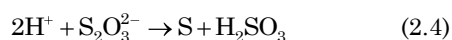
$\text{Na}_2\text{S}_2\text{O}_3$ in an aqueous solution dissociates into 2Na^+ and $\text{S}_2\text{O}_3^{2-}$ by the following reaction:



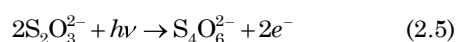
Elemental sulphur S is released when $\text{S}_2\text{O}_3^{2-}$ ions dissociate under irradiation, in an acidic solution of pH 3.6 [12]:



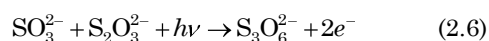
It is known that S is also released from $\text{S}_2\text{O}_3^{2-}$ in an acidic solution by the following reaction



In the presence of UV light $\text{S}_2\text{O}_3^{2-}$ ions liberate electrons:



Similarly electrons are also generated when $\text{S}_2\text{O}_3^{2-}$ ion combines with SO_3^{2-} (sulphite ion) in the presence of UV light:



The $\text{S}_2\text{O}_3^{2-}$ ions act as a reducing agent to form $\text{S}_4\text{O}_6^{2-}$ (tetrathionate) ion or $\text{S}_3\text{O}_6^{2-}$ (trithionate) which supplies electrons for the reduction of Cd^{2+} ions. Cd^{2+} ions combine with elemental sulphur S in the presence of electrons to form CdS at the illuminated region on the substrate:



Fig. 2 – Photograph of PCD experimental arrangement

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

3.1.1 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns of the CdS thin films were recorded in a XPERT PRO X-ray diffractometer operated at 45 kV and 30 mA at $0.03^\circ/1.3$ s in the 2θ range 5.025° - 79.985° using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056$ Å). Fig. 3 shows the X-ray diffractogram of CdS thin films on glass substrate.

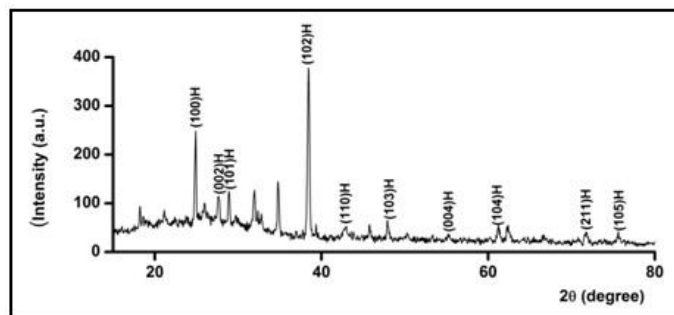


Fig. 3 – XRD pattern of the CdS thin film

The peaks (100), (002), (101), (102), (110), (103), (004), (104), (211) and (105) confirm the hexagonal structure. The grain size value calculated using Scherrer relation [13] is found to be 90 nm.

$$D_c = K\lambda / \beta \cos \theta$$

Where K is the Scherrer's constant, λ is the wavelength of the X-ray, β is full-width at half-maximum (FWHM) and θ is the Bragg angle.

3.1.2 Energy Dispersive X-ray Analysis (EDAX)

Fig. 4 shows the EDAX spectrum CdS thin films. The spectrum exhibit peaks corresponding to presence of cadmium, sulphur of CdS, oxygen of substrate (SiO_2) and carbon (contamination). The atomic percentage of Cd and S are 9.90 and 3.65 respectively.

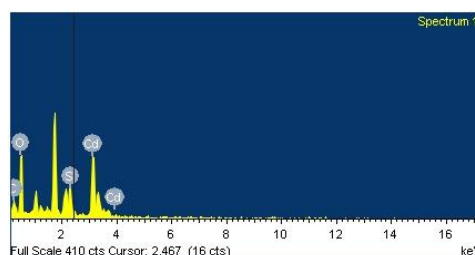


Fig. 4 – EDAX spectrum of CdS thin film

3.2 Optical Analysis

Room temperature optical measurements of CdS thin films are carried out using GBC CINTRA 40 Model UV-VIS spectrophotometer in the wavelength range 200-900 nm. The transmission spectrum of CdS thin films as a function of wavelength is as shown in Fig. 5. The transmittance is found in the range of 47-75%. The actual transmittance of the films is reduced due to the scattering of light on the surface of the CdS film. The calculated bandgap value is found to be 2.35 eV [14].

3.3 Electrical properties

The resistivity of CdS thin films deposited on glass substrate was measured using DC Probe Station 1 (PM5 with Thermal Chuck, Agilent Device Analyzer B1500A) four-point probe technique. The sample used was 1 cm × 1 cm. The resistivity of the film was found to be 1.049×10^6 Ω-cm [15]. The reciprocal of resistivity

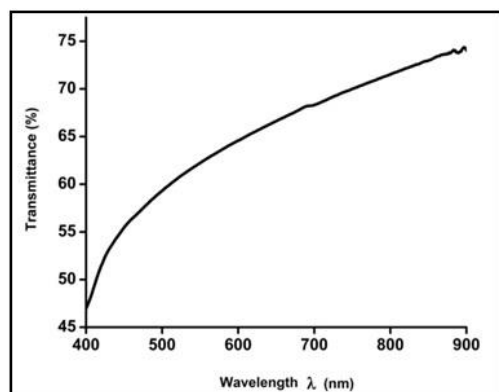


Fig. 5 – Optical transmission spectrum of CdS thin film

gives conductivity of the film. The conductivity of the film is found to be $9.5 \times 10^{-7} (\Omega\text{-cm})^{-1}$. The high resistivity of the CdS films might be due to the grain boundary effects due to the roughness and non-uniformity in the film.

3.4 Atomic Force Microscopy (AFM)

Topography imaging and roughness quantification of CdS thin films were carried out by a Bruker AFM with scanasyst in tapping mode. AFM picture of CdS thin films in 2D and 3D is as shown in Fig. 6 and Fig. 7.

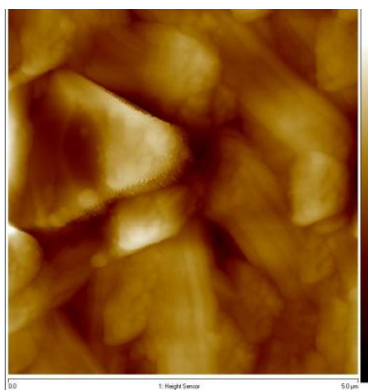


Fig. 6 – AFM 2D image of CdS thin film

Fig. 7 provides the values of rms roughness $R_q = 121$ nm, average roughness $R_a = 96.1$ nm and the

REFERENCES

1. I. Broser, Ch. Fricke, B. Lummer, R. Heitz, H. Perls, A. Hoffmann, *J. Crystal Growth* **117**, 788 (1992).
2. M.E. Calixto, P.J. Sebastian, *Sol. Energ. Mater. Sol. C.* **59**, 65 (1999).
3. U. Pal, R. Silva-Gonzalez, G. Martinez-Montes, M. Gracia-Jimenez, M.A. Vidal, Sh. Torres, *Thin Solid Films* **305**, 345 (1997).
4. J.H. Schon, O. Schenker, B. Batlogg, *Thin Solid Films* **385**, 271 (2001).
5. J. Levinson, F.R. Shepherd, P.J. Scanlon, W.D. Westwood, G. Este, M. Rider, *J. Appl. Phys.* **53**, 1193 (1982).
6. J. Brit, C. Ferekides, *Appl. Phys. Lett.* **62**, 2851 (1993).
7. K.L. Choy, B. Su, *Thin Solid Films* **388**, 9 (2001).
8. G.C. Morris, R. Vanderveen, *Sol. Energ. Mater. Sol. C.* **27**, 305 (1992).
9. N.B. Chaure, S. Bordas, A.P. Samantilleke, S.N. Chaure, J. Haigh, I.M. Dharmadasa, *Thin Solid Films* **437**, 10 (2003).
10. J. Herrero, M.T. Gutierrez, C. Guillen, J.M. Dona, M.A. Martinez, A.M. Chaparro, R. Bayon, *Thin Solid Films* **361-362**, 28 (2000).
11. H.L. Pushpalatha, S. Bellappa, T.N. Narayana Swamy, R. Ganesh, Indian *J. Pure Appl. Phys.* **52**, 545 (2014).
12. Masaya Ichimura, Fumitaka Goto, Eisuke Arai, *Jpn. J. Appl. Phys.* **36**, L1146 (1997).
13. B.D. Cullity, *Elements of X-ray diffraction* (USA: Addison-Wesley Publishing Company, Inc.: 1956).
14. M.A. Mahdi, S.J. Kasem, J.J. Hassen, A.A. Swadi, S.K. J.A l-Ani, *Int. J. Nanoelectron. Mater.* **2**, 163 (2009).
15. R.S. Mane, C.D. Lokhande, *Mater. Chem. Phys.* **65**, 1 (2000).
16. K.K. Nanda, S.N. Sarangi, S.N. Sahu, *Appl. Surf. Sci.* **133**, 293 (1998).
17. G.W. Mbise, G.A. Nikalsson, C.G. Granqvist, *Solid State Commun.* **97**, 965 (1996).

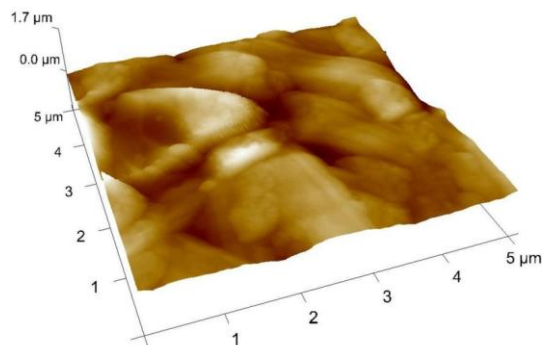


Fig. 7 – AFM 3D image of CdS thin film

Z-max is $1.7 \mu\text{m}$. From the values of Z-max, we conclude that the thickness of the CdS thin film deposited using CdSO_4 source is not more than 1700 nm indicating that the roughness of the film is thickness-dependent, a result in good agreement with earlier reported results [16, 17]. In Fig. 7, the grains of relatively larger size are distributed over the surface uniformly.

4. CONCLUSION

PCD has emerged as a novel technique for deposition of compound II-VI semiconductor thin films offering better control over the deposition on the substrate in aqueous medium. CdS thin films are deposited successfully by PCD. The structural characterization confirms the hexagonal structure. The optical properties reveal a band gap of 2.35 eV. EDAX confirms the presence of Cd and S. AFM gives a Z-max of 1700 nm and electrical resistivity by four-point probe technique is found to be $1.049 \times 10^6 \Omega\text{-cm}$. This work is of fundamental nature from the point of view of suitability for application of the CdS thin film as window material in heterojunction solar cells.

ACKNOWLEDGEMENTS

The authors greatly acknowledges Dr. R Gopalakrishnan, Department of Physics, Crystal Research Laboratory, Anna University, Chennai, Tamilnadu for providing base to carry out research work (PCD experiment). The authors are also thankful to Department of Physics, Indian Institute of Science (IISc), Bangalore for providing XRD facility.