

Structural and Optoelectronic Properties of Nanocrystalline CdTe Thin Films Synthesized by Using SILAR Technique

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Nanocrystalline CdTe thin films were deposited on amorphous glass substrate using successive ionic layer adsorption and reaction (SILAR) technique. The films are characterized using XRD, FESEM, optical absorption techniques and electrical resistivity measurement. The XRD pattern revealed that nanocrystalline CdTe thin films has mixed phase of hexagonal and cubic crystal structure. The calculated crystallite size from the XRD measurement was found to be in the range of 9-12 nm. FESEM image showed uniform deposition of the material over entire glass substrate and film consists of interconnected spherical grains of nanometer size. Compositional analysis showed that the nanocrystalline CdTe thin film becomes cadmium deficient and tellurium richer. The optical absorption studies show that the films have a direct band gap of 1.51 eV. The room temperature resistivity of the synthesized nanocrystalline CdTe films measured by two probe method was found to $6.64 \times 10^4 \Omega \cdot \text{cm}$.

Keywords: SILAR, Cadmium Telluride, XRD, FESEM, Optoelectronic properties.

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1. INTRODUCTION

Binary compound semiconducting materials has been extensively studied in the last few decades in order to find new suitable materials for the fabrication of low cost and high efficiency thin film solar cells [1]. Cadmium telluride (CdTe) belonging to II-IV compound semiconductors has attracted attention of many researchers for fabrication of the thin film solar cells [2]. Because of a direct band gap of the order of 1.45 eV and high absorption coefficient ($\sim 10^5 / \text{cm}$) in the visible region, CdTe material in thin film form have attracted considerable attention as potential material for realization of high efficiency solar cell [2, 3]. Also nanocrystalline CdTe thin films are important because of their potential applications in semiconducting devices, solar cells and photovoltaics, radiation detectors, optoelectronic devices, sensors and nano-devices etc. [4].

CdTe thin films have been deposited by a variety of techniques such as chemical bath deposition [5], electrodeposition [6], spray [7], vacuum evaporation [8], sputtering [9], pulsed laser deposition [10], magnetron sputtering [11], closed space sublimation [12], physical vapor deposition [13], thermal evaporation [14, 15] and screen printing [16] etc. Among all the available deposition techniques, successive ionic layer adsorption and reaction (SILAR) is an attractive technique that has widely employed for thin film deposition, which is based on the immersion of the substrate into separately place cationic and anionic precursors and rinsing between every immersion with ion exchange water to avoid homogeneous precipitation [17]. This technique is suitable for coating conducting as well as non-conducting sub-

strate surfaces to achieve good quality thin films and has been employed to fabricate several metal chalcogenide and oxide semiconductor thin films [18, 19]. Keeping these advantages of SILAR technique in mind and only a few reports are available in the literature on the deposition of CdTe thin films by SILAR method, herein we report the study of structural and optoelectronic properties of nanocrystalline CdTe thin films synthesized by using SILAR technique.

2. EXPERIMENTAL DETAILS

2.1 Substrate Cleaning

Initially amorphous glass substrates of the size $75 \text{ mm} \times 25 \text{ mm} \times 2 \text{ mm}$ were washed with double distilled water (DDW), boiled in chromic acid for 2 h. Again, the substrates were washed with detergent, rinsed in acetone and finally ultrasonically cleaned with double distilled water before deposition of thin film.

2.2 CdTe Film Formation

Cadmium acetate [$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], tartaric acid [$(\text{CHOH} \cdot \text{COOH})_2$], hydrazine hydrate [$\text{H}_2\text{N} \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$], ammonia [NH_3] and Sodium tellurite [Na_2TeO_3] were used in the deposition of CdTe thin films.

The cationic precursor for CdTe was 0.3 mol l^{-1} cadmium acetate complexed with tartaric acid at $\text{pH} \sim 5$. The source for tellurium ions was 0.24 mol l^{-1} sodium tellurite along with hydrazine hydrate which is

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a reducing agent and ammonia. Ammonia was added for the decomposition of hydrazine and prevention of the precipitation of tellurium compounds. Hydrazine hydrate reduces the tellurium valency from Te^{4-} to Te^{2-} , which is a favorable condition for the formation of CdTe in the presence of Cd^{2+} ions at 333 K temperature. The pH of the anionic precursor was ~ 12.1 .

The cationic precursor which is solution of cadmium acetate is kept at room temperature (300 K) and the anionic precursor was maintained at 333K throughout the experiment. The adsorption and reaction time in growth of CdTe thin film was 35 s and rinsing time was 30 s. Thus a single SILAR deposition cycle consisted of 35 s of adsorption of Cd^{2+} ions then 30 s of rinsing with double distilled water, 35 s adsorption and reaction of Te^{2-} ions with preadsorbed cadmium ions on the glass substrate and then again rinsing with double distilled water for 30 s. At the end, the first SILAR growth cycle is completed. For this particular study we have deposited CdTe thin films with 30 SILAR cycles. After 30 SILAR cycles an adherent and uniform thin CdTe thin film of thickness 200 nm is obtained on the glass substrate.

2.3 Characterization of CdTe Thin Films

The thin films of CdTe were characterized for structural, morphological, optical and electrical properties. The CdTe film thickness was measured by weight difference method. X-ray diffraction (XRD) pattern of the film were recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20-80°

(2θ) using CuK_α radiations with wavelength 1.5405 Å. The surface morphology and composition was studied by scanning electron microscopy (FESEM) and energy dispersive spectrometer (EDS). To study the optical characteristics of the nanocrystalline CdTe film, absorbance spectra was recorded in the range 500-1100 nm by means of JASCO V-630 UV-Vis spectrophotometer. The resistivity of the CdTe thin films was determined by the standard two-probe method.

3. RESULTS AND DISCUSSION

3.1 Thickness Measurement Studies

Nanocrystalline CdTe thin films were grown onto amorphous glass substrate under optimised conditions. All the optimized preparative parameters used for the SILAR deposited CdTe thin films are summarized in Table 1. In order to study the thickness measurement study, nanocrystalline CdTe thin films were deposited for various SILAR cycles on amorphous glass substrates.

After deposition of the CdTe thin films with various SILAR cycles, the films thickness was measured by employing gravimetric weight difference method. Fig. 1 represents CdTe film thickness as a function of the SILAR cycles. Film thickness was found to be about 200 nm for 30 cycles. Growth rate was found to be about 6.7 nm per cycle. It is found that the film thickness increases linearly with the deposition cycles up to 30 SILAR cycles; afterwards, film thickness was decreased due to the peeling off the outer powdery layer [20].

Table 1 – Optimized preparative parameters used for synthesis of cadmium telluride thin film

Deposition condition	Cationic precursor	Anionic precursor
Chemicals used	Cadmium acetate, Tartaric acid	Sodium tellurite, Hydrazine hydrate, ammonia
Concentration	0.3 mol l^{-1} [$\text{Cd}(\text{CH}_3\text{OO})_2 \cdot 2\text{H}_2\text{O}$] + tartaric acid	0.24 mol l^{-1} [Na_2TeO_3] + HH (2ml) + ammonia
pH	5	12.5
Immersion time(s)	35	35
Rinsing time (s)	30	30
Temperature (K)	300	333

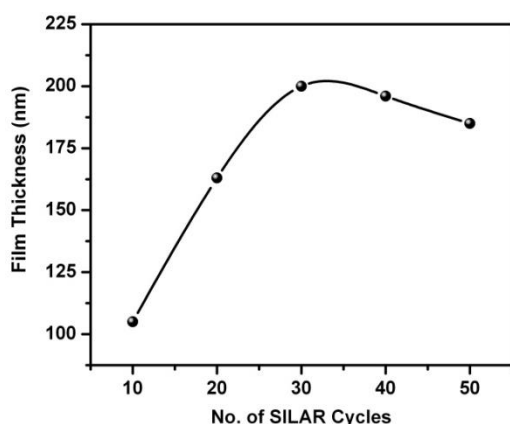


Fig. 1 – Variation of thickness of the of nanocrystalline CdTe thin film as a function of SILAR cycles

3.2 Structural Analysis

The nanocrystalline CdTe thin films were uniform and grayish in colour. The XRD spectrum of the nanocrystalline CdTe film deposited onto the glass substrate is shown in Fig. 2.

The sample exhibits several obvious XRD peaks corresponding to the planes (102), (111), (420) and (214) based on JCPDS card no. 80-0090 and 75-2083. XRD patterns revealed that the deposited thin films are nanocrystalline in nature with mixed phase of hexagonal and cubic crystal structure. Appearance of peak at $2\theta = 37.33^\circ$ is due to presence of impurity CdO_2 . For the peaks corresponding to $2\theta \approx 29.09^\circ$ and 43.59° observed in XRD pattern, we calculated the crystallite size using Scherrer's formula [21].

For nanocrystalline CdTe thin films, the calculated crystallite size from the XRD measurement was found to be in the range of 9-12 nm.

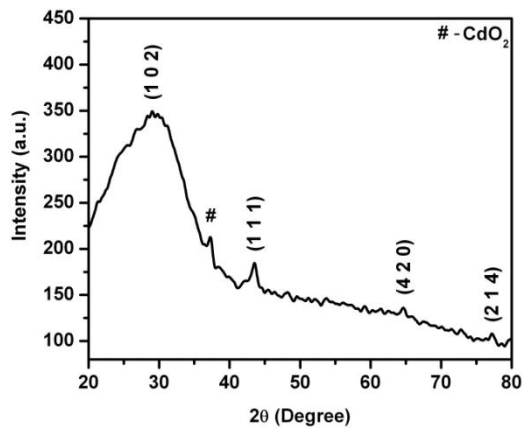


Fig. 2 – XRD pattern of nanocrystalline CdTe thin film synthesized by using SILAR technique

3.3 Surface Morphology and Compositional Studies

FESEM images for as deposited nanocrystalline CdTe thin films on glass by using SILAR technique were taken to study the surface morphology. Fig. 3 shows the FESEM image of nanocrystalline CdTe thin films deposited by using SILAR on glass substrate. The micrographs reveals that the film is well adherent, homogeneous and well covered to the substrate surface without any cracks and pinholes and deposited film consists of interconnected spherical grains mostly falling in nanometer regime. Kokate et. al. [22] reported similar kind of morphology for CdTe thin film synthesized from aqueous acidic bath using electrodeposition technique.

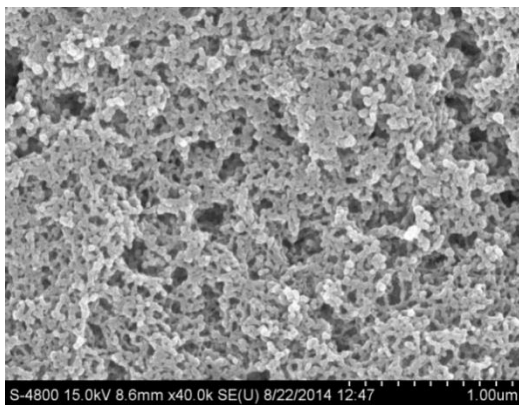


Fig. 3 – FESEM image of nanocrystalline CdTe thin film synthesized by using SILAR technique

The quantitative analysis of the film was carried out by using the EDS technique for SILAR grown nanocrystalline CdTe thin films deposited on a glass substrates in order to study the stoichiometry of the film. The elemental analysis was carried out only for Cd and Te and it has been found that the nanocrystalline CdTe film becomes cadmium deficient and tellurium richer.

3.4 Optical Properties

The optical properties of the nanocrystalline CdTe

films were measured by using UV-Vis spectrophotometer at room temperature in the wavelength range of 500-1100 nm. The variation of optical absorbance with wavelength which is shown in Fig. 4, was analyzed to find out the nature of transition involved and the optical band gap.

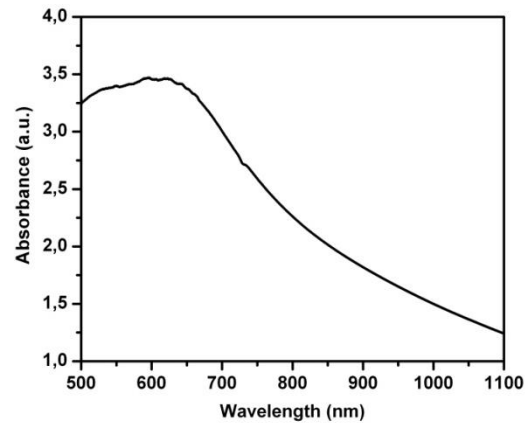


Fig. 4 – Absorbance with respect to wavelength for nanocrystalline CdTe thin film synthesized by using SILAR technique

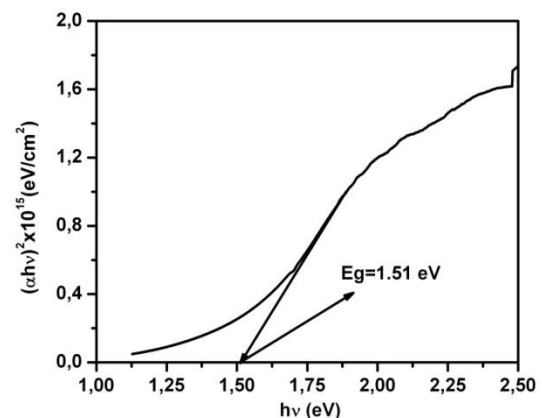


Fig. 5 – Plot of $(\alpha hv)^2$ versus hu for nanocrystalline CdTe thin film synthesized by using SILAR technique

The theory of optical absorption gives the relation between the absorption coefficient α and the photon energy $h\nu$, especially, for direct allowed transition as,

$$\alpha = \frac{A(h\nu - E_g)^2}{h\nu} \quad (1)$$

where $h\nu$ is the photon energy, E_g is the optical band-gap, A is a constant.

A typical plot of $(\alpha hv)^2$ versus $h\nu$ for 30 SILAR immersion cycles deposited nanocrystalline CdTe thin films is as shown in Fig. 5. The linear fit of the plot indicates the existence of the allowed direct band-gap transition.

By extrapolating the straight line portion to the $h\nu$ axis for zero absorption coefficient (α), the band gap energy was determined. The optical band gap energy was found to be 1.51 eV for the as grown nanocrystalline CdTe thin film having thickness 200 nm on the glass substrate. This value of band gap was in good agreement with the earlier reported value of band gap for electro-synthesized CdTe thin films for 50 minute [6].

3.5 Electrical Studies

The measurements on electrical resistivity of the nanocrystalline CdTe thin film synthesized by SILAR technique was carried out in the temperature range 300-423 K on rectangular-shaped samples with typical size of 1.2 cm × 1.2 cm, using a standard two point probe method. The variation of log ρ versus inverse of absolute temperature ($1000/T$) for the films deposited with 30 SILAR cycles, shown in Fig. 6. The resistivity of the films decreases with increase in temperature indicates semiconducting nature of the films [23]. The resistivity of the films synthesized with 30 SILAR cycles was found to be $6.64 \times 10^4 \Omega \cdot \text{cm}$.

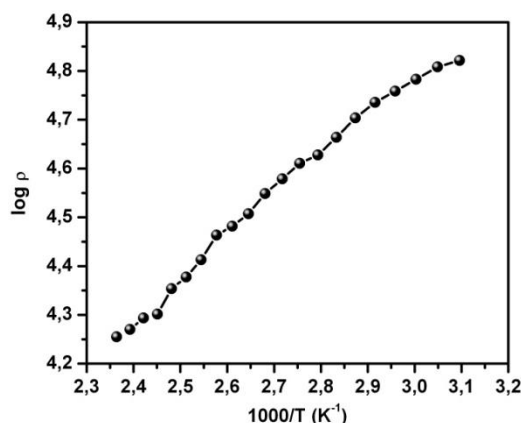


Fig. 6 – Plot of logarithmic resistivity versus the inverse of temperature for nanocrystalline CdTe thin film synthesized by using SILAR technique

Generally, activation energy E_a is determined by using the following Arrhenius relation,

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right).$$

REFERENCES

- S. Chander, M.S. Dhaka, *Phys. E: Low-dimen. Syst. Nanostr.* **73**, 35 (2015).
- R.K. Sharma, G. Singh, A.C. Rastogi, *Sol. Energy Mater. Sol. Cells* **82**, 201 (2004).
- R. Zia, F. Saleemi, S. Nasseem, *Opt.* **127**, 1972 (2016).
- A.A. Al-Ghamdi, S.A. Khan, A. Nagat, M.S. Abd El-Sadek, *Opt. Laser Technol.* **42**, 1181 (2010).
- K.M. Garadkar, S.J. Pawar, P.P. Hankare, A.A. Patil, *J. Alloys Compd.* **491**, 77 (2010).
- İ. Şişmana, Ü. Demir, *J. Electroanal. Chem.* **651**, 222 (2011).
- V.V. Ison, A. Ranga Rao, V. Dutta, *Solid State Sci.* **11**, 2003 (2009).
- S.J. Ikhmayies, R.N. Ahmad-Bitar, *Physica B* **405**, 3141 (2010).
- Y.O. Choi, N.H. Kim, J.S. Park, W.S. Lee, *Mater. Sci. Eng. B* **171**, 73 (2010).
- P. Hu, B. Li, L. Feng, J. Wu, H. Jiang, H. Yang, X. Xiao, *Surf. Coat. Technol.* **213**, 84 (2012).
- M.A. Islam, M.S. Hossain, M.M. Aliyu, M.R. Karim, T. Razykov, K. Sopian, N. Amin, *Thin Solid Films* **546**, 367 (2013).
- J.D. Major, Y.Y. Proskuryakov, K. Durose, S. Green, *Thin Solid Films* **515**, 5828 (2007).
- K.K. Chin, Z. Cheng, A.E. Delahoy, *J. Cryst. Growth.* **418**, 32 (2015).
- S. Chandramohan, R. Sathyamoorthy, S. Lalitha, S. Senthilarasu, *Sol. Energy Mater. Sol. Cells.* **90**, 686 (2006).
- E.R. Shaaban, N. Afify, A. El-Taher, *J. Alloys Compd.* **482**, 400 (2009).
- H. Yao, J. Ma, Y. Mu, S. Su, P. Lv, X. Zhang, L. Zhou, X. Li, Li Liu, W. Fu, H. Yang, *J. Alloys Compd.* **634**, 19 (2015).
- C.D. Lokhande, B.R. Sankapal, H.M. Pathan, M. Muller, M. Giersig, H. Tributsch, *Appl. Surf. Sci.* **181**, 277 (2001).
- H.M. Pathan, C.D. Lokhande, *Bull. Mater. Sci.* **27**, 85 (2004).
- S.M. Pawar, B.S. Pawar, J.H. Kim, Oh-Shim Joo, C.D. Lokhande, *Curr. Appl Phys.* **11**, 117 (2011).
- S.D. Sartale, C.D. Lokhande, *Mater. Chem. Phys.* **72**, 101 (2015).
- H. Moualkia, S. Hariech, M.S. Aida, N. Attaf, E.L. Laifa, *J. Phys. D: Appl. Phys.* **42**, 135404 (2009).
- A.V. Kokate, M.R. Asabe, P.P. Hankare, B.K. Chougule, *J. Phys. Chem. Solids*, **68**, 53 (2007).
- A.A. Yadav, M.A. Barote, E.U. Masumdar, *Solid State Sci.* **12**, 1173 (2010).

Note that the symbols have usual meaning.

The values of activation energy E_a was found to be in 0.164 eV. The value of the activation energy indicates that the prepared sample is a semiconductor.

4. CONCLUSION

It is concluded that preparation technique as simple as successive ionic layer adsorption and reaction (SILAR) is effectively feasible for the preparation of thin films of II-VI compound semiconductors such as CdTe. The good quality nanocrystalline CdTe thin films mainly obtained at the optimum deposition parameters such as concentrations of cationic and anionic precursors, number of SILAR cycles, immersion and rinsing time etc. From XRD studies, it is confirmed that obtained films has mixed phase of hexagonal and cubic crystal structure and films are nanocrystalline in nature. The FESEM image showed that the film is dense, uniform and homogeneous with interconnected spherical shaped grains with a crack free appearance. From EDS study the prepared film is found to be Te rich. Optical study revealed that the optical band gap of the nanocrystalline CdTe film deposited on the glass substrate is 1.51 eV. Electrical resistivity measurement study showed that the prepared thin films have very good semiconducting properties which results its utilization in photovoltaic cell.

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