TechnoChem
International Journal of TechnoChem Research
ISSN:2395-4248 www.technochemsai.com
Vol.02, No.01, pp 84-89, 2016

Influence of Dipping Cycle on Physical Properties of Nanocrystalline CdO Thin Films Prepared by SILAR Method

M. Karunakaran[1]*, K. Rubanancy[1], M. Rajini[1], G. Kavitha[1] and R. Chandramohan[2]

[1]Department of Physics, Alagappa Government Arts College, Karaikudi – 630 003, India.
[2]Department of Physics, Sree Sevugan Annamalai College, Devakottai - 630 303, India.

Abstract : Cadmium oxide (CdO) thin films were prepared by successive ionic layer adsorption and reaction (SILAR) method by altering dipping cycle. The prepared films were annealed at 250^0C for 2 h. The prepared films were characterized by X-ray diffraction (XRD), optical spectroscopy and scanning electron microscopy (SEM) measurement. The XRD analysis reveals that the films were polycrystalline with cubic structure. Both crystallinity and the grain size were found to increase with increasing dipping. SEM analysis shows the porous nature of the surface with spherical nano clusters. Energy dispersive spectroscopic analysis (EDX) confirmed the presence of Cd and O elements. The films exhibited maximum transmittance (50% - 75%) in infra-red (IR) region. The estimated band gap energy (Eg) was in the range of 2.0 eV - 2.2 eV.

Keywords: Thin films, Silar, X-ray diffraction, Crystallite size, Glass Substrate and Optical band gap.

Introduction

Transparent conducting oxides (TCOs) are potential candidates for energy efficient devices like solar cells, light emitting diodes, photo detectors because of their high transparency in the visible region and high electrical conductivity at room temperature [1]. Various oxides such as SnO_2, In_2O_3, ITO, FTO, and CdO are used as transparent electrodes in solar cells and other optoelectronic devices [2]. Cadmium oxide (CdO) is an II-VI compound n-type degenerate semiconductor with a simple cubic structure having a direct band gap of 2.3 eV [3]. Deposition techniques such as sputtering [4], metal-organic chemical vapor deposition (MOCVD) [6], pulsed laser deposition (PLD) [5], chemical vapor deposition (CVD) [7], spray pyrolysis [9], sol-gel technique [8], chemical bath deposition (CBD) [10] and successive ionic layer adsorption and reaction (SILAR) [11] technique have already been employed to prepare CdO thin films. Among these deposition techniques, SILAR has many advantages such as low cost, simplicity and reproducibility. Moreover anion and cation precursor in different baths offers good control over the deposition parameters such as pH, deposition temperature and time, etc [12]. The only disadvantage of this technique is the formation of hydroxide phase while oxide growth and slow growth rate. In this work, CdO thin films were prepared by SILAR method and the influence of dipping cycle on the structural, optical and transport properties of the CdO thin films are discussed in detail.

Experimental Procedure

CdO thin films were prepared using a modified SILAR technique involving double dip. CdO thin films were grown using a two-step modified SILAR using a solution comprising 0.05 M cadmium acetate [$Cd(CH_3COO)_2.2H_2O$) (99% e-Merck), 0.2 ammonium hydroxide with a pH value of 7±0.2 deposited at bath temperature of 90 °C under optimized condition. The complexing agent ammonium hydroxide was used to

stabilize the crystallite size. In a modified SILAR all the precursor solutions are taken in a single beaker [13]. Before deposition, the glass substrates were cleaned in hot chromic acid followed by cleaning with an alkali and acetone. The well-cleaned substrates were immersed in the chemical bath for a known standardized time followed by immersion in hot water for the same time for hydrogenation. The process of solution dip (step 1) followed by hot water dipping (vary step 2) is repeated for known number of times such as 10, 15 and 20 cycle. The cleaned substrate was alternatively dipped for a predetermined period in ammonium cadmium bath and water bath kept at room temperature and near boiling point, respectively. The thickness of the coated films was measured using the surf test SJ – 301 stylus type surface roughness and thickness measuring instrument. X-ray diffraction analyses were obtained using the model X"pert PRO (Analytical) X-ray powder diffractometer with Ni filtered CuKα (1.54056 Å) radiation. The surface morphology and homogeneity of the deposited films were studied by SEM model JSM 35 CF JEOL. Optical absorption measurement in the range 300 – 1100 nm was carried out by using a Hitachi – 3400 UV-Vis-NIR Spectrophotometer. The CdO thin film formed was confirmed by XRD (Rigaku Ultima III) analysis and the micro structural analyses of the samples were performed using SEM (JEOL Model JSM - 6390LV).

XRD Studies

Figure 1 (a - c) shows the XRD pattern of the CdO thin films deposited using different dipping cycles of 0.05 M. All the diffraction peaks of XRD pattern could be indexed to cubic crystal structure of CdO, which is in good agreement with the standard data for CdO (JCPDS data file no. 78-0653). This is in accordance with the reports on CdO thin films prepared by SILAR method [14]. The grown CdO have exhibited strong orientation along (1 1 1) plane [15-16] and also it has shown reflections along (2 0 0), (2 2 2) planes too. The intensity of the diffraction peak was also found to increase with increasing dipping cycle and get sharper with decreasing full width half maximum (FWHM). This can be attributed to the improvement in crystallinity of CdO thin films. This can be attributed to the improvement in crystallinity of CdO thin films. But 10 dipping cycle only (1 1 1) plane was appears. No other peaks were appearing.

The structural parameters of CdO thin films are given in Table 1. The crystallite size is calculated using Debye - Scherrer's formula [17-19]

$D = k\lambda / \beta \cos\theta$ ----------→ (1)

Where k is the shaping factor which takes value from 0.89 to 0.94, 'λ' is the wavelength of the Cu-k_α line, 'β' is the full width at half maxima (FWHM) in radians and 'θ' is the Bragg's angle.

Dislocation density (δ) for (111) plane is evaluated using the relation

$\delta = 1/D^2$ ----------→ (2)

The strain (ε) is calculated from the following relation

$$\varepsilon = \left(\frac{\lambda}{DCos\theta} - \beta\right)\frac{1}{\tan\theta} \quad \text{----------→ (3)}$$

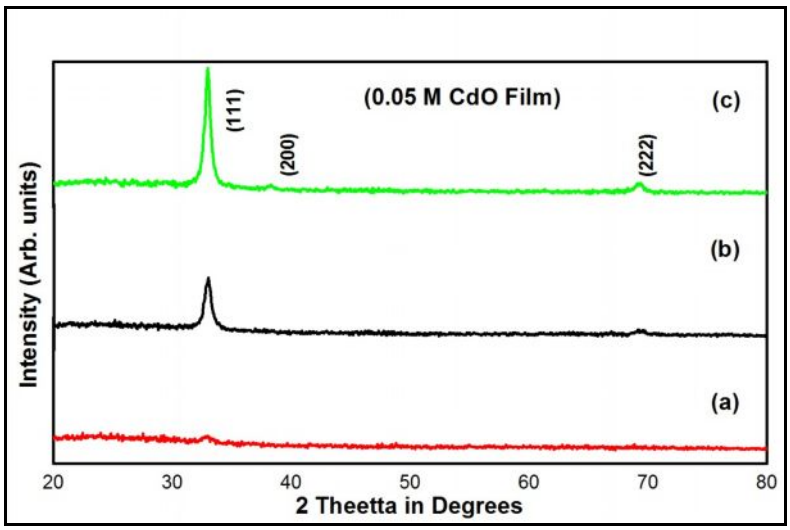


Fig. 1: CdO thin films of 0.05 M at (a) 10 dip (b) 15 dip (c) 20 dip

Table 1. Microstructural properties of various dipping cycle prepared CdO thin films

Cadmium acetate concentrations (M)	No. of Dipping	Crystallite size (D) nm	Micro strain (ε) x 10^{-3}	Dislocation density δ x 10^{15} lines/m^2
0.05	10	8.65	0.136	0.1336
	15	18.75	2.844	2.844
	20	24.11	1.720	1.720

Morphological studies:

The surface morphology of the CdO thin films was investigated by using scanning electron microscope. Fig.2 (a-c) shows the SEM micrographs of CdO thin films prepared at various dipping cycle such as 10, 15 and 20 with 0.05 M of solution concentration. SEM micrograph reveals the presence of uniformly sized spherical nanoclusters distributed over the surface. The surface of the film is found to be heterogeneous, having porous surface with small pinholes. Those were formed by bigger particles agglomerated randomly and found that there is no uniform shape. Such image is compact and relatively not dense. This kind of micro structure is desirable for sensor applications.

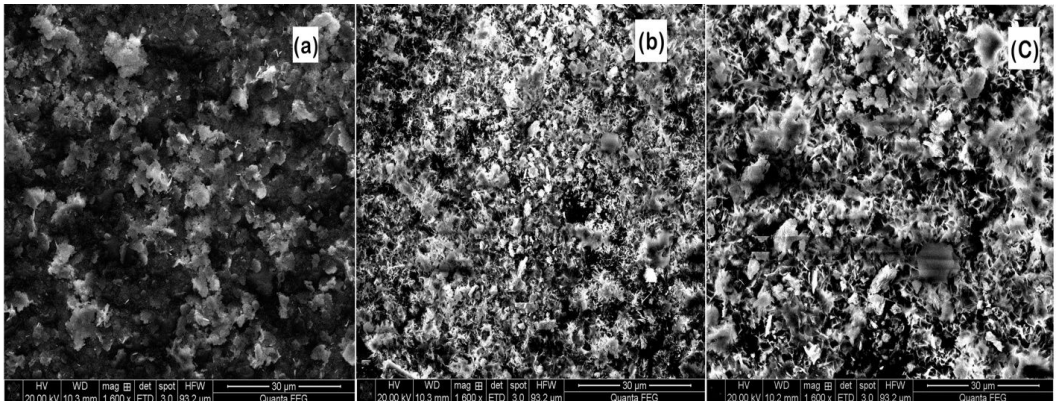
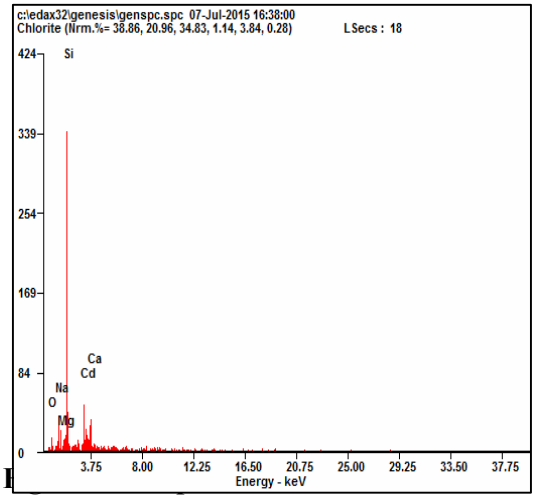


Fig 2 (a-c): SEM micrograph of CdO thin films (a) 10 dip (b) 15 dip (c) 20 dip

Elemental Analysis:



Elemental analysis of CdO thin films was carried out by EDX. Fig. 3 represents the EDX spectrum of CdO thin film. EDX analysis confirms the presence of Cd and O elements in the prepared CdO film.

Optical Studies:

UV-Visible Spectroscopy

Fig.4 (a-c) shows the optical transmittance spectra of the CdO films deposited using different dipping cycles of the precursor solutions 0.05 M in the wavelength range of 350-1200 nm. The dipping cycle of CdO in the films could have markedly affected the optical properties of the grown films. The film coated with 15 dipping cycle of molarity 0.05 M has shown a high transmittance of 75 % and it has been gradually decreased with the increase of dipping in the SILAR. This reduction of the transmittance might be due to the increase in thickness of the films with the concentration of cadmium acetate. It is also been noticed that, there is slight shift of optical absorption edge towards red region as the dipping increases, it suggest that there is a decrease in the optical band gap (*Eg*). The sharp absorption edge obtained for all the films has clearly shown the crystalline quality of the films. The absorption coefficient (α) can be calculated from the transmittance (T) values from the Lambert law.

$$\alpha = \frac{In(1/T)}{t} \quad \text{----------} \rightarrow \quad (4)$$

The variation of absorption coefficient with photon energy (hv) takes the form [33], where *Eg* is the band gap, '*A*' is a constant related to the effective masses associated with the bands and n is a constant which is equal to one for a direct- gap material and four for an indirect-gap material. To decide whether the CdO films have direct or indirect bang gap, $(\alpha hv)^2$ *vs. (hv) and* $(\alpha hv)^{1/2}$ *vs. (hv)* plots are drawn. Since better linearity is obtained in the $(\alpha hv)^2$ *vs. (hv)* plot, the direct band gap values are determined by extrapolating the linear portion of this plot to the energy axis (Fig.5).

$$\alpha = A(hv - Eg)^{n/2} \quad \text{----------} \rightarrow \quad (5)$$

The band gap value of the film is found to change between 2.0 eV - 2.2 eV. The direct optical band gap values obtained from various methods are in the range of 2.4, 2.54 eV for CdO films for sputtering, 2.3, 2.5 eV for spray pyrolysis, 2.3, 2.63 eV for chemical bath deposition, and 2.42 eV for sol–gel technique [20-25]. The obtained E_g values for the studied CdO films are lower than the values obtained those methods, which might be due to increased crystallite size and thickness of the films with higher concentration. This indicates that the optical band gap of the CdO film can be controlled by dipping.

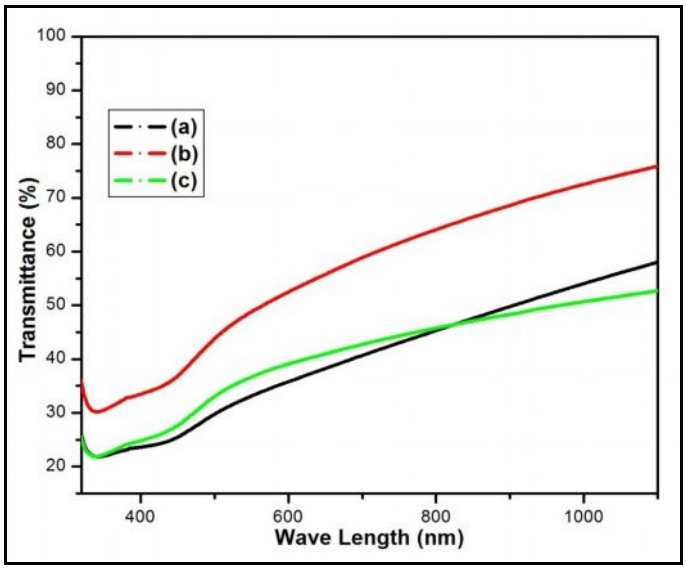


Fig 4: Transmission spectra for CdO thin films (a) 10 dip (b) 15 dip (c) 20 dip

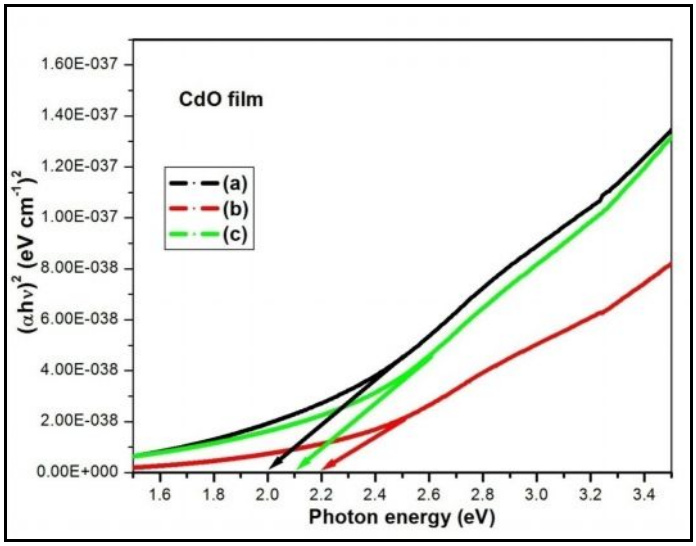


Fig 5: Optical Band Gap CdO thin films (a) 10 dip (b) 15 dip (c) 20 dip

Conclusion

Nanocrystalline CdO thin films were fabricated by modified SILAR method by altering dipping cycle. XRD studies show that all the films are polycrystalline in nature with cubic structure having preferential orientation along (1 1 1) plane. It is observed from the SEM images and XRD patterns that the grain sizes of the structures were increased with dipping cycle. The optical transmittance in the visible range is greater than 75%. The optical band gap of the coated CdO films increase with the increase in dipping cycle. Both optical band gap and morphological properties could be controlled and calibrated by adjusting the dipping cycle. This controlling mechanism might be instrumental for different optoelectronic device applications where tunable material properties including bandgap and crystalline quality are of critical importance. We believe that our proposed SILAR based nano structured CdO film coating technique is promising for tunable opto electronic materials synthesis.

References

1. B. Saha, S. Das, K.K. Chattopadhyay, Sol. Energy Mater. Sol. Cells 91 (2007) 1692-1697.
2. K. Gurumurugan, D. Mangalaraj, S.K. Narayandass, C. Balsubramanian, Phys. Stat. Sol. 143 (1994) 85-91.
3. T.K. Subramanyam, G. Mohan Rao, S. Uthanna, Mater. Chem. Phys. 69 (2001) 133-142.
4. K. Gurumurugan, D. Mangalaraj, Sa.K. Narayanadass, J. Cryst. Growth 147 (1995) 355-360.
5. Z. Zhao, D.L. Morel, C.S. Ferekides, Thin Solid Films 413 (2002) 203-211.
6. R.K. Gupta, K. Ghosh, R. Patel, S.R. Mishra, P.K. Kahol, Mater.Lett. 62 (2008) 4103-4105.
7. X. Liu, C. Li, S. Han, J. Han, C. Zhou, Appl. Phys. Lett. 82 (2003) 1950-1952.
8. R. Ferro, J.A. Rodriguez, Thin Solid Films 347 (1999) 295-298.
9. R. Maity, K.K. Chattopadhyay, Sol. Energy Mater. Sol. Cells 90 (1995) 597-606.
10. A.J. Varkey, A.F. Fort, Thin Solid Films 239 (1994) 211-213.
11. M.A. Yilidirim, A. Ates, Sens. Actuators A 155 (2009) 272-277.
12. B. Gokul, P. Matheswaran, R. Sathyamoorthy J. Mater. Sci. Technol., 2013, 29(1), 17-21.
13. M. Karunakaran, R. Chandramohan, S. Balamurali, S. Gomathi, K. Kabila, T. Mahalingam, Int. J. Thin Fil. Sci. Tec. **3**, No. 2, (2014) 61-65
14. R.J. Deokate, S.M. Pawar, A.V. Moholkar, V.S. Sawant, C.A. Pawar, C.H. Bhosale, K.Y. Rajpure, Appl.Surf.Scie.254 (2008) 2187–2195.
15. N.Manjula, A.R.Balu, Int. J. Che. Phy. Sci. 3, (2014),54–62.
16. G.Shanmugavel, A.R.Balu, V.S.Nagarethinam, Int. J. Chem. Mater. Res. 2, (2014), 88–101,
17. B.D. Cullity, Elements of X-Ray Diffraction, Addison-Wesley Publications Company Inc, Reading, Massachusetts, 1956.

18. S. Valanarasu, V. Dhanasekaran, M. Karunakaran, R. Chandramohan, T. Mahalingam J. Nanosci. Nanotechnol.13, (2013) 1–6,
19. V. Dhanasekaran, T. Mahalingam, Mater. Res. Bull. 48, (2013) 3585–3593.
20. Gurumurugan, K., Mangalaraj, D., Narayandass, Sa.K., Sekar, K., Girija Vallabhan, C.P., 1994. Semicond. Sci. Technol. 9, 1827.
21. Chu, T.L., Chu, S.S., 1990. J. Electron. Mater. 19, 1003.
22. Sravani, C., Reddy, K.T.R., Reddy, P.S., Jayarama Reddy, P., 1994. J. Mater. Sci. Lett. 13, 1045.
23. Varkey, A.J., Fort, A.F., 1994. Thin Solid Films 239, 211
24. Gurumurugan, K., Mangalaraj, D., Narayandass, S.K., Balasubramanian, C., 1994. Phys. Status Solidi A 143, 85
25. Najadoski, M.Z., Grozdanov, I., Minceva Sukarova, B., 1996. J. Mater. Chem. 65, 761.

*****