Study on Structural and Optical properties of CdO:Al thin films Deposited by Spray Pyrolysis Method

RAM PRASANTH.R, KUMARESAN.D, ARAVIND. D, KESAVAN.K.

Department Of Physics

Periyar Maniammai University Vallam, Thanjavur – 613403.

Abstract- **The Transparent Conducting Oxides [TCO] extensively investigated materials for photovoltaics and opto-electronic systems. Transparent Conducting Oxide for diverse application in Photovoltaic and Opto-electric devices. Aluminium doped CdO thin films were deposited on cleaned glass substrates with different concentrations of aluminium at a substrate temperature 300°C. The deposited films were characterized by studying their structural and optical properties. The X-ray diffraction pattern revealed that the films are in polycrystalline phase and their grain size was obtained by Debye – Scherrer formula. Optical parameters such as absorption, transmittance and band gap were obtained using UV-Vis Spectrophotometry. Transmittances of the thin films were found to be 85% in the visible region. Scanning Electron Microscope [SEM] image displays the Surface Morphology of thin films. The thickness of the film was between 1.14µm-1.60µm.**

Keywords: Spray pyrolysis, Al:CdO thin films, structural, morphological and optical properties

I.INTRODUCTION

Transparent conducting oxides [TCO] have various applications in advanced technologies like flat panel, Photo voltaic devices anti reflection coating materials and solar energy systems. Among several TCOs, CdO is one of the important materials for the fundamental studies. CdO films have been successfully used for many applications like high electrical conductivity, high visible – NIR optical transmittance [1], large energy band gap and remarkable luminescence characteristics in visible spectral region [2] due to their peculiar combination. These CdO are n-type semiconductors with the band gap within 2.2-2.8 eV and has low resistivity ($10^{-2} – 10^{-4}$ Ωcm) owing to the defect of oxygen voids and cadmium interstitials [3]. Further CdO films are used in Liquefied Petroleum Gas [LPG] sensors the sensitivity and electrical conductance of film are consistent [4]. Various doping elements such as Ge [5], Cr[6],Mg[7], Ce [1] etc. Al is a notable dopant in ZnO thin films. Yet very few reports were made in Al-doped CdO thin films [8-10]. Several methods were incorporated on preparation of Al doped CdO thin film such as Spray Pyrolysis[11],Radio Frequency Magnetron Sputtering (RF Sputtering) [12], Sol-Gel spin coating [13], Dip coating [3], metal–organic chemical vapour deposition (MOCVD) [14], Thermal evaporation [15]. The spray pyrolysis since it is relatively simple, economically vast area coating and best suited for formation of fine grain, chemically homogenous nanostructure films. In this paper Al doped CdO films were deposited on glass by homemade chemical spray pyrolysis method. The above mentioned observations were kept in mind, in the present study, the effect of molarities of Al on the structural, Optical and Morphological properties of CdO films are investigated in detail.

II. EXPERIMENTAL DETAILS

Aluminium doped CdO thin films were incorporated on micro-slide glass substrates employing homemade chemical spray pyrolysis unit. Cadmium Acetate dehydrate ($Cd(CH_3COO).2H_2O$) was used as precursor for Cd with uniform molarity of 0.05M for all coating. Aluminium Chloride ($AlCl_3$) was applied as precursor for Al for varying molarity of 0.01M-0.05M. Both the precursor was mixed together in solvent of deionized water. The glass substrates

were soaked in Aqua Regia (3:1 Nitric acid and Hydrochloric Acid) and cleaned with Methanol and rinsed with deionized water. The temperature of the substrate was maintained at 300°C. The spray rate was 3ml/sec in the successive spray method. The nozzle is fixed at an angle 45° and 35cm distance to the substrate, with the pressure of 2 torr for getting fine mist of spray. The temperature of the substrate is controlled by thermocouple.

The crystalline structure of the films was examined using PANaltical X-ray Diffractometer, using Cu-Kα radiation of wavelength

1.540×10^{-10}m.
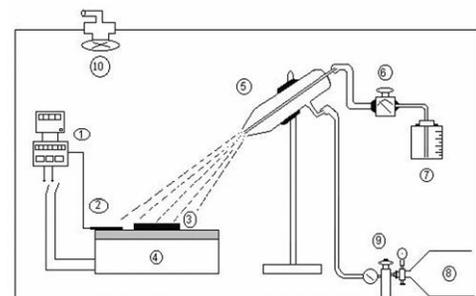
1. Thermostat   2. Thermocouple   3. Substrate
4. Plate heater   5. Spray gun   6. Flow meter
7. Solution reservoir   8. Air compressor tank   9. Pressure regulator
10. Exhaust fan

Figure 1: Simplified diagram of home built spray pyrolysis unit.

The optical studies were carried out by spectrophotometry in UV-Vis region. Surface studies were carried out by Scanning Electron Microscope (Tscan- SEM).

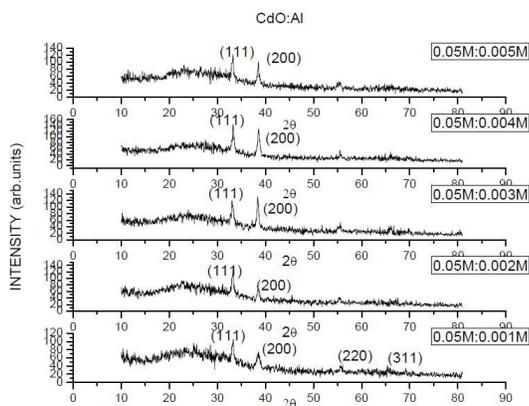III. RESULT AND DISCUSSION

A. STRUCTURAL ANALYSIS

Fig. 2: XRD pattern of various concentration of Al doped CdO thin films with different concentrations.

The XRD patterns of the thin films are shown in figure 2. From this result, the existence of multiple diffraction peaks of (111), (200), (220) and (311) planes indicates the polycrystalline nature of the CdO compound with cubic rock salt structure of the CdO samples on the basis of comparison with JCPDS (Joint Council of Powder Diffraction Data) card No: 005-0640.

CdO:Al shows a preferential growth along (111) direction. Aluminium doping causes increase in the intensity of the (111) reflection. With the 0.003M Aluminium doping a slight increase in the intensity of (200) reflection which may be due to the fact that aluminium being with comparable radius of oxygen, it may occupy the interstitial space which are oxygen vacancies. The preferential orientation is changed from (111) plane to (200) plane for the doping concentration of 0.004M. In the higher concentration of Aluminium, there is again an increase in the intensity of (111) reflection compared to (200). In the concentration of Aluminium at 0.003M there is a tremendous increase in the intensity of (200) reflection. As the concentration of Al is increased the intensity is found to be reduced. The grain size (ζ) was also calculated using Debye-Scherrer formula for the preferential plane (111).

However, intensity of all peaks rapidly decreases and full width at half maximum (FWHM) increases for the films with high Al content (9 %). This behaviour can be associated with the presence of Al-Cd compounds in the amorphous phase and with a diminishing of the CdO grain size. The lattice parameter decreases from 4.66858 to 3.05277Å when Al percentage increases from 0 to 9 %.

$$\zeta = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

Where, ζ is the crystalline size, 0.9 is a constant, λ is wavelength of X-Ray, β is the Full Width at Half Maximum (in radians) and θ is the Bragg angle.

The grain size decreased rapidly upon increasing the Al concentration. The grain size of the 0.001M film was found to be $4.16 \times 10^{-8}m$ respectively .which increased to in the range of 4.16×10^{-8} - $1.12 \times 10^{-7}m$ for 0.002 – 0.005M of aluminium.
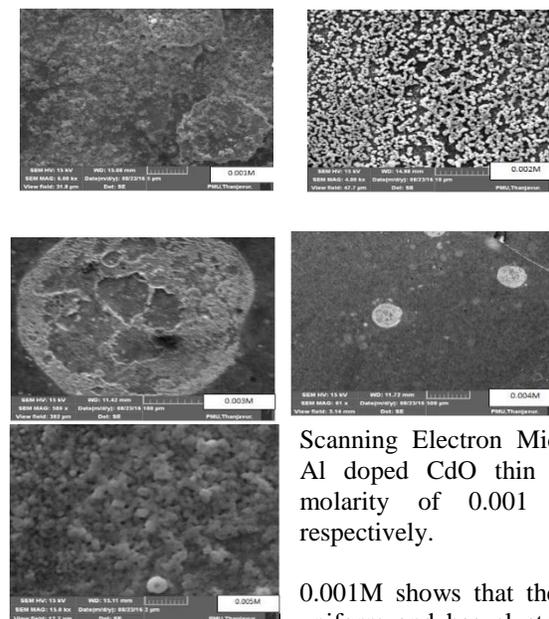
B.SURFACE MORPHOLOGY

Fig. 3.

Scanning Electron Micrograph of Al doped CdO thin films from molarity of 0.001 - 0.005M respectively.

0.001M shows that the surface is uniform and has clusters in them.

Clusters have higher energy than the individual atoms [16]. Coating has good adhesiveness of the film on the substrate.

In 0.003M CdO:Al film contains intermolecular spaces between them these intermolecular space can be viewed visually, this may lack in continuity and conductivity properties. However, 0.005M film is highly dense may have high continuity and conductivity. This can be due to at higher temperature growing adjoins with each other and form island stage and appear as spheroid shape Films with 0.002M have grains composed of smaller crystallines this structure repeats throughout the material with closely packed to each other, film contains intermolecular spaces between them these intermolecular space can be viewed visually, this may lack in continuity and conductivity properties.

This may be due to lesser decomposition which leads to voids in the films. 0.003M with droplet slashes due to less adhesive of the film .some spheroid shape appears on the film surfaces, this may be because of colloidal particles formed in the solution then absorbed on the film[17]. 0.004M of CdO:Al thin film have plane uniform coating which resulted in high reflection in XRD peak.

C. OPTICAL PROPERTIES

The UV - Vis spectrophotometer reading shows the absorbance and transmittance of CdO:Al film prepare at optimized condition. It shows slight increase in transmission above 450 nm. Owing to the crystalline property of the prepared thin film a smooth increase is found. A maximum transmission 84.71 is found at 691 nm. The absorption coefficient α is calculated from lambert's law:

$$\alpha = \frac{2.303\,A}{t} \qquad (2)$$

Where 'A' is optical absorbance and 't' is the thickness of the film. The film thickness is measured by Profilometer. The notable result of the study is that as the Al doping concentration increases, the absorption edge of CdO:Al thin films were found to decrease from $1.7\ m^{-1}$- $0.9 m^{-1}$. This may be due to greater the cluster of molecule has great tendency to absorbance.
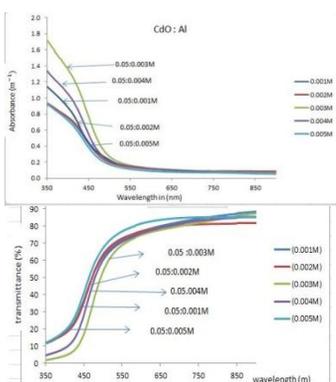

Figure 4: Absorbance and Transmittance spectra of CdO Films with various Al doping molarities.

Increasing the doping concent-ration decreases the absorption window. The highest trans- mittance is showed by the CdO : Al film with Aluminium concentration of 0.005M. The figure shows that all the films have transmission about 80-85% in the visible range. Conversely, the absorbance vs wavelength graph figure 4 shows that a sharp descend in the absorbance occurs at for the 0.001M film. From the figure 4, 0.001M CdO thin films transmit at 470nm but doped CdO thin films begins to transmit at 410nm. The 0.005M of Al in thin film sample shows the lowest absorbance at about $0.8 m^{-1}$ whereas, the

0.005M Al doped CdO thin films have enhanced higher transmission window in the lower range of 450-500nm. 0.005M has 85.7% maximum and the transmission window is reduced at 475nm Thus the Aluminium doping increases the optical transparency is increased. From plot between $(\alpha h\nu)^2$ and hν as shown in figure 5 direct allowed band gap were determined. The increase in the Al concentration, results in

sharp raise of optical band gap is clearly seen in figure 4. Thickness of the film also plays vital role in determining the bandgap of thin films. Band gap is usually obtained by extrapolations of the one – dimensional portion of the plots o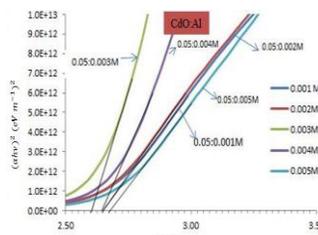f $(\alpha h\nu)^2$ *vs* hν, as shown in Figure 5. The graph is extrapolated to give bandgap value is found to be 2.6eV – 2.675eV as the dopant concentration increases the band gap increases this increase in band gap may be due to moss Burstein effect.

D. CONCLUTION

Using spray pyrolysis method, both aluminium doped CdO thin films were deposited and compared. Structural study using X - ray diffractometer shows that all the thin films made were polycrystalline and cubic shaped structure and preferential crystal growth along (111) direction. SEM analysis reveals the surface morphology of various doped and un-doped CdO thin film in which doping of 0.005 M has more density and high continuity. It is suitable for large area production good photovoltaic conversion efficiency. The optical studies were done using UV-Vis spectrophotometer which shows increase in the transparency of light in the visible region, as the Aluminium concentration increases, the transparency was found to increase up to 85%. Also, with doping, there is a small change in the band gap. Thus doping with Aluminium gives better transparent conducting oxide thin film which can be utilized in the photovoltaic industry etc. from overall point of view it can be considered an advantage that so many avenues exist that potentially lead to a low cost solar cell. Therefore CdO:Al thin film can be used for anti-Reflection Coating in thin film solar Cells.

REFERENCE:

1. P. Velusamy, R. Ramesh Babu, K. Ramamurthi, M. S. Dahlem, E. Elangovan, RSC Advances., Vol. 124, (2015).
2. Zenhe J. Rahem Mohammed, A. Salih, Auday H. Ahmed, Energy Procedia, Vol.36, P. 42-49, (2013).
3. R. Kumaravel, S. Menaka, S. Regina Mary Snega, K. Ramamurthi, K. Jeganathan, Materials Chemistry and Physics, Vol.122,P. 444–448, (2010) .
4. R.R. Salunkhe, D.S. Dhawale, D.P. Dubal, C.D. Lokhande, Sensors and Actuators B Vol. 140, P.86, (2009).
5. A. A. Dakhel, Advances in Opto Electronics, Vol. 2013, P.1-6, (2013).
6. B. Hymavathi, B. Rajesh Kumar, T. Subba Rao, Procedia Materials Science, Vol.10, P.285 – 291, (2015).

7. K. Usharani, A.R.Balu, V.S.Nagarethinam, M.Suganya, Progress in Natural Science: MaterialsInternational, Vol.25, P. 251-257, (2015).
8. V. Saravanan, J. Joseph Prince, Journal of Ovonic Research Vol. 11, No. 5, P.213 – 219 (2015).
9. S. J. Helen , Suganthi Devadason , T. Mahalingam, J. Mater. Sci: Mater. Electron, (2016).
10. Ramiz Ahmed Al-Ansari, IOSR Journal of Applied Physics,Vol. 8, P. 06-15, (2016).
11. M.K.R. Khan, M. Azizar Rahman, M. Shahjahan, M. Mozibur Rahman, M.A. Hakim, Dilip Kumar Saha, Jasim Uddin Khan, Current Applied Physics Vol.10 ,P. 790–796, (2010).
12. Bong Ju Lee and Jin Jeong , Journal of Spectroscopy, vol.2016 (2016).
13. S. Ilican, M. Caglar, Y. Caglar, Optoelectron. Adv. Mater. Rapid Commun. Vol.3, P. 135, (2009).
14. A.W. Metz, J.R. Ireland, J.G. Zheng, R.P.S.M. Lobo, Y. Yang, J. Ni, C.L. Stern, V.P. Dravid, N. Bontemps, C.R. Kanne wurf, K.R. Poeppelmeier, T.J. Marks, J. Am. Chem. Soc. Vol.126, P 8477–8492, (2004).
15. N. Wongcharoen, T. Gaewdang, T. Wongcharon, International Conference on Materials for Advanced Technologies 2011,Symposium O. Energy Procedia, vol. 15, P. 361, (2012).
16. A.Hasnat and J.Podder, Journal of Bangladesh academy of sciences, vol. 37, no.1, 33-41, 2013.
17. A.Hasnat and J. Podder, Advances in material physics and chemistry vol.2, 226-231, 2012.