International Journal of Chemical Engineering and Applications, Vol. 1, No. 2, August 2010
ISSN: 2010-0221

Characterization of CdO Thin Films Prepared By SILAR Deposition Technique

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***Abstract*—Cadmium oxide thin films were deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) method using as a source material of cadmium acetate and ammonium hydroxide solution on glass substrate. The effect of molarity is one of the important factors, which determines the quality of films. The present study determines the effect of molarity of solution on the structural, optical and morphological properties of as deposited films. XRD and SEM reveal that the crystallite size is increased with increase in molarity of precursor solution. UV-VIS spectrum of the films showed that the optical band gap energy increases with concentration of cadmium acetate in the precursor solution.**

***Index Terms*—thin film; CdO; silar: xrd; SEM; optical**

I. Introduction

The actual and potential applications of Transparent Conducting Oxides (TCO) thin films includes for window defrosters [1], Light emitting diodes, semiconductor lasers, transparent electrodes for flat panel displays and photovoltaic cells. The availability of the raw materials and economics of the deposition method are also significant factors in choosing the most appropriate TCO material. The n-type transparent conducting oxides such as tin oxide [2], zinc oxide [3], cadmium oxide [4-6] etc., cadmium oxide is the wide range of applications as solar cells, windows, flat panel display, photo transistors etc.[7-8]. Cadmium oxide thin films prepared by various techniques, spray pyrolysis [9-11], r.f.sputtering [12], solution growth [10] etc., have been reported. In SILAR technique the substrate is immersed into separate cation and anion precursor solutions and rinsed with purified water after each immersion. The SILAR deposition offers many advantages for the fabrication of thin films including ease of compositional modification, control of stoichiometry of precursor solution, feasibility of deposition on large-area substrates and inexpensive equipments. The variation of solution molarity of precursor affects the hydrolysis and condensation behavior of the solution, which in turn influences the structure of the resultant film. The aim of this work is to produce cadmium oxide thin films by means of the SILAR technique and to investigate their structural, optical and morphological properties and this dependence on solution molarity.

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II. Experimental

Cadmium oxide thin film deposition on glass substrates from aqueous solution of cadmium acetate [$Cd(CH_3COO)_2.2H_2O$ 99.99%] in two different molarity of 0.03M and 0.06M using SILAR technique. A detailed procedure of this technique used for the thin film growth has been reported many researchers [13]. Different molarities of solutions were prepared by mixture of cadmium acetate (cation) and ammonium hydroxide. The complexing agent ammonium hydroxide was used to stabilize the crystallite size. The pH of the prepared solution was measured and found to be 6.5 and 8.5 at 0.03M and 0.06M of cadmium acetate mixture. Films produced with high acidic solution (pH<6) and more basic solution (pH>9) shows poor quality after deposition. The glass substrate was cleaned by chromic acid followed by distilled water rinse. The cleaned substrate was immersed first in cadmium acetate (0.03M) and ammonium hydroxide solution for 30 s, and then immersed in quantitative amount of double distilled water in 15s at 95˚C. The glass substrate was immersed in 0.003M of Hydrogen peroxide (anion) solution for 30s, and then immersed in double distilled water in 15s maintained at the same temperature. The same experiment is conducted by only changing the molarity of cation and anion of precursor solution. This cycle was repeated several times in order to increase the overall film thickness of CdO. In this way, the substrate was covered with a thin layer of the complex solution. The overall reaction process can be expressed as decomposition of cadmium acetate to form cadmium oxide when placed in Hydrogen peroxide as part of the CdO was deposited onto the substrate as a strongly adherent film and they appeared in dark yellowish colour. The deposited film was subsequently annealed in air at 300°C for 45 minutes. Film thickness was determined by weighing method using the formula,

$$t = m / A \rho \qquad (1)$$

Where ‘t’ is the thickness of the film, ‘m’ is the weight gain, A is the area of the coated film and ρ is the density of CdO. The film thickness was determined to be approximately 0.95 and 1.45 μm for the solution molarity of 0.03 and 0.06M. And it shows the molarity increases the thickness of the as deposited films also increases. And also the thickness of film is verified with cross sectional view of SEM image. The structural study was determined by X-ray diffractrometer (Rigaku Model RAD II A) with Cukα radiation (α-1.541 Å). The surface morphologies of the films were determined by using Scanning Electron Microscope (JEOL 1600). Prior to imaging, the films were

sputtered with thin gold film to enhance the emission of secondary electron for better imaging. Optical transmittance was measured by UV-VIS single beam spectrophotometer (ELICO-159).

III. Results and Discussion

A. Structural Properties

XRD pattern of cadmium oxide films were studied at room temperature. Figure (1) shows that the crystalline pattern of as deposited films (0.03M and 0.06M of CdO) on clean glass substrate. Observation of the film shows smooth surface and well adhesive nature of the film with substrate. The peak observed in all the diffractrogram confirms the polycrystalline nature of the CdO films. The peaks are appear due to diffraction from (111), (200) and (222) cubic phase formation as compared with standard X-ray diffraction data file [JCPDS file No. 75-0594], while comparing the X-ray diffraction pattern of 0.03M and 0.06M of CdO, it is obvious that, Bragg's peaks became more intense for higher molarity indicating a clear improvement in crystallinity. Thus the XRD results confirms that by using SILAR technique CdO films can be prepared at low temperature than that of the other conventional solid state reaction method. The grain sizes is estimated using Scherrer relation,

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

Where K is a constant (0.94), λ is the wavelength of CuKα line, θ is the Bragg's angle and β is full width half maximum (FWHM) of the preferential plane. The mean crystallite size calculated using Scherrer formula for 0.03M and 0.06M of CdO is found to be 45nm and 62nm.

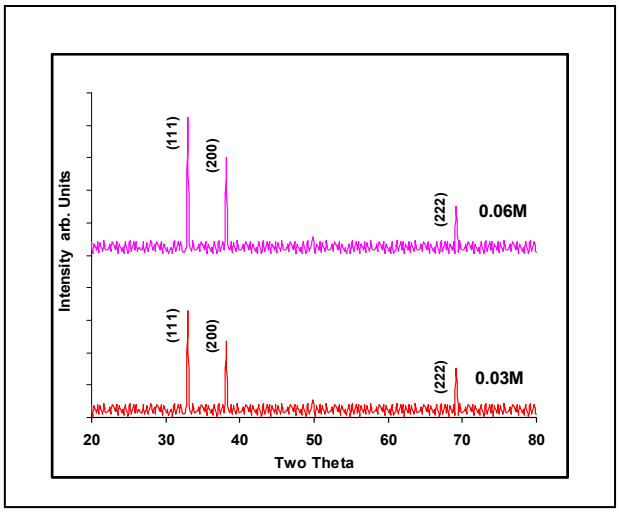

Figure 1. XRD pattern of CdO thin films

B. Optical Properties

Transmittance spectra recorded for CdO films as a function of wavelength range 400-1000nm is as shown in Figure (2). The plot shows a sharp rise in transmittance near the band edge attributed to the good crystallinity of the film [14]. And it shows a narrow range of variation with increase in molarity of precursor solution.

It is observed that the transmittance decreases with increase in molarity of precursor solution. The film deposited with 0.03M shows higher transmittance compare to 0.06M. This property of high transmittance makes it a good material for optical coatings. The optical band gaps of the films are calculated from the transmittance spectra employing Tauc's plot. The absorption coefficient (α) is calculated using the equation, [15]

$$\alpha = \ln (1/T) / d \quad (3)$$

Where T is transmittance and d is film thickness. The absorption coefficient (α) and the incident photon energy (hν) is related by the following equation, [16]

$$(\alpha h\nu)^2 = A (h\nu - Eg) \quad (4)$$

Where A and Eg are constant and optical band gap respectively. The experimental accuracy of the absorbance is ± 0.005 and the wavelength is ±0.05nm. The observed absorbance data were corrected relatively to optically identical uncoated glass substrate.

The absorption spectra of the CdO with molarity of 0.03M and 0.06M prepared at 95˚C were recorded as a function of wavelength range 400nm - 1000nm with glass as the reference is shown in Figure (3). It shows the representatives of optical absorbance which reveals that the absorbance of the film decreases gradually with increase in wavelength. All of the films deposited at the various molarities displayed high transparency in the visible regions with little or no difference in optical transparency.

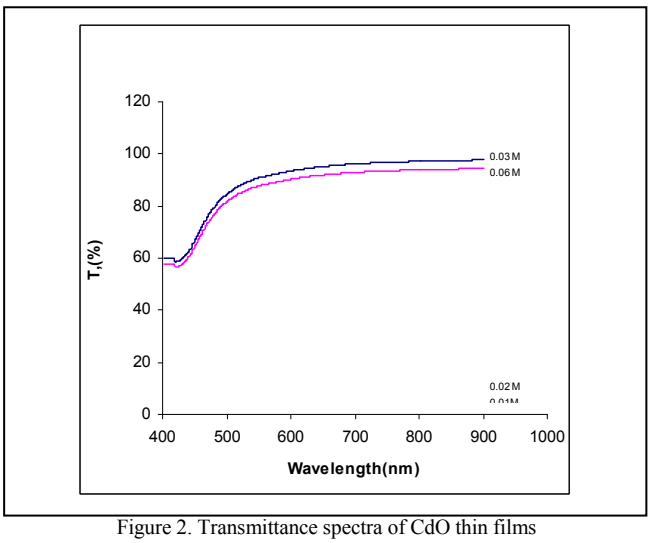

Figure 2. Transmittance spectra of CdO thin films

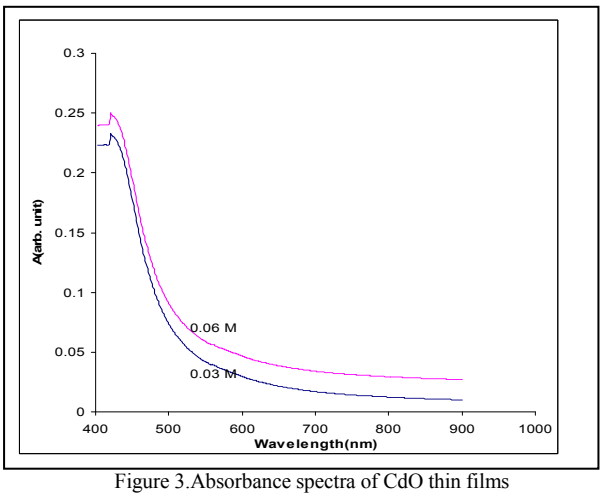

Figure 3.Absorbance spectra of CdO thin films

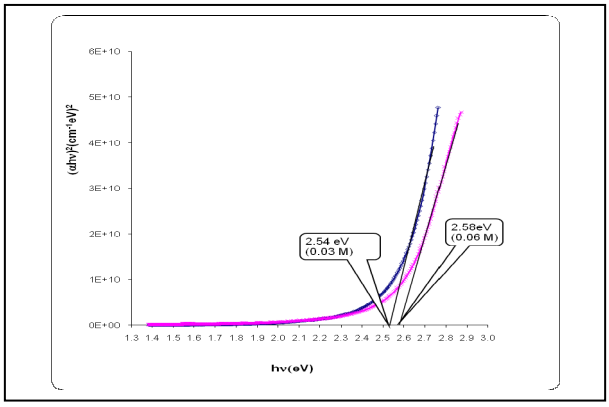

Figure 4. Tauc's plot for CdO thin films

It is clear from the graph that, in the visible region there is no significant change in band edge by increasing the molarity of the solution from 0.03M - 0.06M. This implies that the basic crystal structure is not changed. The typical plots of $(\alpha h\nu)^2$ versus hν for CdO thin films with 0.03M and 0.06M deposited on glass substrate is shown in Figure (4). It is observed that increase in molarities of CdO precursor solution yields a slight increase in optical band gap from 2.54ev to 2.58ev.

C. *SEM Analysis*

The SEM micrograph of the thin film deposited on a clean glass slide is taken using cold field emission of SEM (JEOL, JSM 6701F, Japan). Prior to the observation, using an auto sputter fine coater (JFC 1600, JEOL Japan) about 50Å gold was sputtered on the thin film surface for better contrast and to avoid charge accumulation. SEM micrograph of the cadmium oxide thin film is prepared by two different molarities is taken to support the XRD observations.

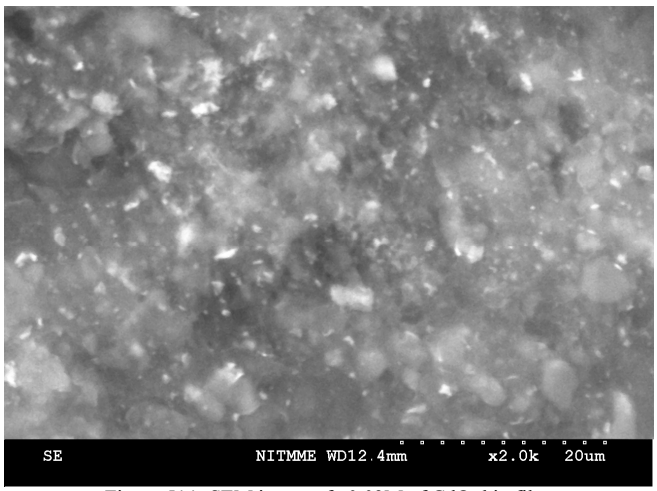

Figure 5(a). SEM image of 0.03M of CdO thin film

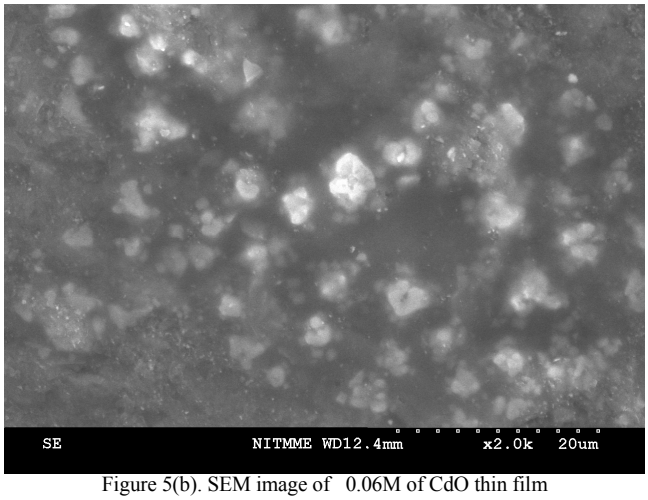

Figure 5(b). SEM image of 0.06M of CdO thin film

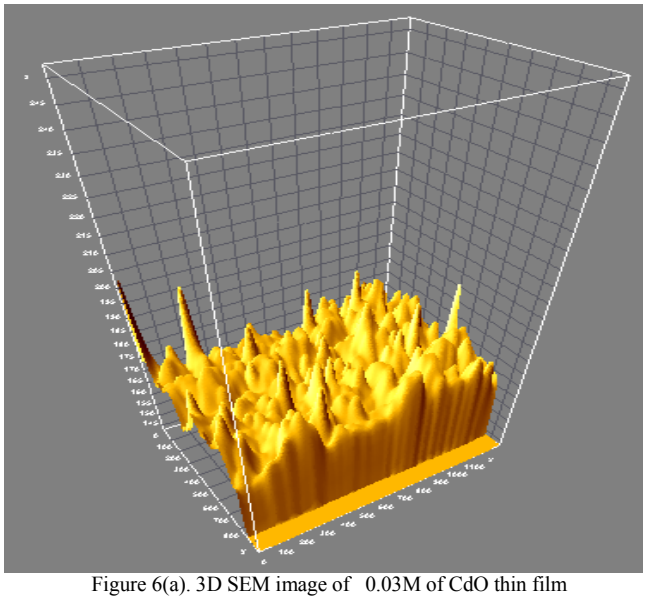

Figure 6(a). 3D SEM image of 0.03M of CdO thin film

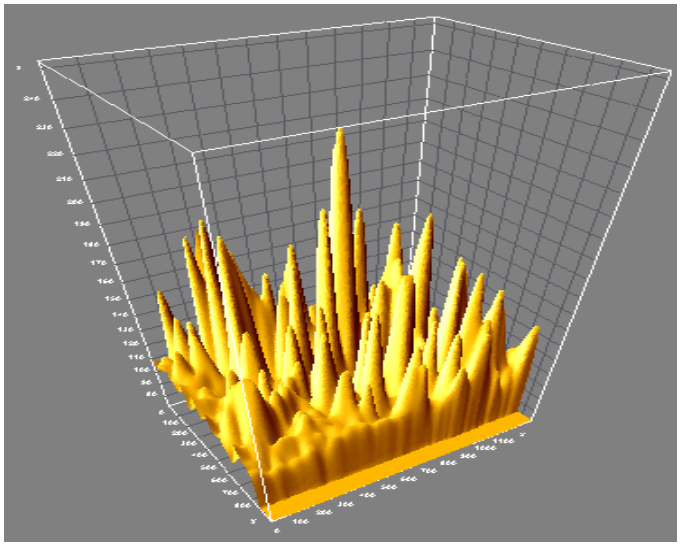

Figure 6(b). 3D SEM image of 0.06M of CdO thin film

Fig. 5(a) & 5(b) shows the SE micrograph shows the surface topography of the deposited films. The film 0.06M of precursor solution Fig.5 (b) have larger particle size of than that of 0.03M Fig.5 (a). The size of the grains increased as the molarity of the precursor solution increases. The higher molarity of cadmium oxide thin films showed

compact distribution over the surface and good connectivity between grains.

The SE micrograph have been further analyzed by a 3D image processing software and the results have been obtained for 0.03M and 0.06M of CdO film is shown in Fig. 6(a) and 6(b). This technique confirms the crystalline structure improves in higher molarity of as deposited film. And it shows the faceted columnar microstructure of the film is perpendicular to the surface. Here shadowing is very prominent and the columns are elongated along the preferential growth direction.

IV. CONCLUSIONS

Cadmium oxide thin films of different molarities were successfully deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) method on glass substrate by maintains the temperature of the Hydrogen peroxide at 95ºC. The present study determines the effect of molarity of solution on the structural, optical and morphological properties of as deposited films. XRD pattern confirm the films shows the polycrystalline nature of the film with preferential orientation along (111) plane. The Optical studies carried out on the films reveals that the film deposited in higher molarity are of low transmittance and high absorbance nature. It also shows that as the molarity increases band gap increases. XRD and visual inspection of SEM picture reveals that the crystallite size is increased with increase in molarity of precursor solution.

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