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Archives of Physics Research, 2014, 5 (6):43-48
(http://scholarsresearchlibrary.com/archive.html)

ISSN : 0976-0970
CODEN (USA): APRRC7

Study of structural, optical and electrical properties of CdO thin film deposited by sol-gel spin coating technique

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ABSTRACT

Nanocrystalline transparent conducting CdO thin films were grown onto glass substrates by simple and economical sol-gel spin coating method. The structural, electrical, optical properties and morphological properties of the deposited films were investigated by X-ray diffractometry, dc resistivity measurements, UV-Vis transmission and absorption spectroscopy and scanning electron microscopy respectively. XRD studies revealed that CdO films are nanocrystalline in nature with cubic lattice. The variation of electrical resistivity with temperature conforms that films are semiconducting in nature. The optical characterization showed that nanocrystalline CdO film exhibits 3.42eV band gap energy which is attributed to quantum size effect.

Key words: *thin film, nanocrystalline, chemical synthesis.*

INTRODUCTION

Transparent conducting oxides (TCOs) are the solid state oxides with low electrical resistivity and high optical transparency in visible range on electromagnetic spectrum. Because of these properties they have wide range of applications in optical and electrical devices, such as solar cells [1], light emitting diodes, flat panel displays, photo transistors and gas sensors etc[2]. The most important property of TCOs is that, they reflect I.R light up to high extent which makes them applicable in smart windows [3-7]. Besides this CdO rhombus and cauliflower like structures are used as a water purifier for the absorption of cango red dye from water [11, 12]

CdO is widely studied n-type nonstoichometric semiconducting metal oxide with low electrical resistivity of 10^{-2}-10^{-4}Ω cm [3,8] ,high transparency to visible light up to 82% [10],and optical band gap varying between 2.2 to 2.7 eV [9,10].The physical properties discussed above have remarkable dependence on the size of the crystallite that varies depending on synthesis method. Also the various deposition parameters such as substrate temperature [13], post annealing[14], concentration of solution [15], complexing reagent [16, 17] and PH [18] etc. affects it's physical and chemical properties. The various nanostructures of CdO such as nano wires, nano rods, quantum dots etc. were synthesized in order to improve the properties of bulk CdO and their applications [19−21]. Up till now the CdO thin films were deposited using number of techniques such as spray pyrolysis [22],Chemical bath deposition [23],Chemical vapor deposition [24], thermal evaporation technique [2], SILAR [12], ball milling [26], salvo thermal method [27], sol gel spin coating [14], dip coating [25], pulsed filter cathodic arc deposition [28] etc.

In the present work an attempt has been made to deposit nanocrystalline CdO thin films by sol- gel spin coating technique using cadmium acetate di-hydrate, monoethanolamine and 2-methoxyethanol. The structural, morphological, electrical and optical properties of CdO films were studied and reported.

MATERIALS AND METHODS

Before actual deposition the glass substrates were boiled in concentrated chromic acid for 30 minutes and then kept them in it for next 48 h at room temperature. The slides were then washed with liquid detergent and distilled water. Finally the slides were cleaned by ultrasonic cleaner for 10 minutes and dried in air.

CdO nanocrystalline thin films were deposited onto precleaned glass substrate by sol-gel spin coating method using cadmium acetate di-hydrate as a cadmium source. Here 2-mathoxyethanol and monoethanolamine were used as a solvent and stabilizer respectively. To prepare sol, 10 gm of cadmium acetate di-hydrate was dissolved into 25 ml of distilled water, in which 10 ml of 2-methoxyethanol was mixed with constant stirring. Finally, 0.3 ml of monoethnolamine was added drop by drop in it, to get homogeneous and transparent sol. As prepared sol was then kept at ambient for next 24h to get gel. This gel was then further diluted by adding appropriate amounts of monoethanolamine and distilled water. The as prepared solution was then spin coated on glass substrate at 1200 rpm using the homemade spin coating apparatus for 30s.Theas deposited glass substrates were then dried at constant temperature 423 K for 10 h to remove solvent and impurity traces. These films are further annealed for half hour at 613 K to obtained faint yellowish transparent CdO thin film.

The structural characterization was carried out on Philips PW 1710 diffractometer with CuKα radiation of wavelength 1.5406 $A^0$and the data was used to investigate crystallographic and microstructural parameters. The surface morphological studies were carried out using a JEOL 6380 A scanning electron microscope. The optical characteristics were studied using a Lambda 25 UV–VIS spectrophotometer (PerkinElmer). The electrical resistance measurements were carried out in the temperature range 303–443 K using the two-probe method. To determine type of conductivity, thermo-emf measurements were carried out. The temperature gradient was maintained along the length of the film and the potential difference across the terminals having a separation of 1cm was measured with the help of digital micro-voltmeter.

In present work, thickness of the film was measured by using relation,

$$t = \frac{m}{A\rho} \qquad (1)$$

Where, m is the mass of the film deposited onto the substrate, A is the area of the deposited film and ρ is the bulk density of CdO (8.15 g/cm^3). The thickness of CdO film grown by sol-gel spin coating technique is around 476 nm.

RESULTS ANDDISCUSSION

Structural analysis

Fig. 1 shows XRD pattern of CdO thin film. The observed data is compared with standard data [JCPDS- 75-0593]. The (111), (200), (220) and (311) peaks are due to cubic CdO. The crystallite size of deposited CdO material was estimated by using scherrer formula [29],

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

Where K is shape factor generally taken as 0.94, β is (FWHM) full width at half of maximum intensity in radian, θ is Bragg's angle in radian, λ is wavelength of CuKα radiation used (1.5406 A^0).

The various crystallographic and microstructural parameters such as lattice constant (a), strain (ε), dislocation density (δ) and number of crystallites associated with preferential peak (N), texture coefficient (TC) were estimated by using relations,

$$\text{lattice constant (a)} = \frac{d}{\sqrt{h^2+k^2+l^2}} \qquad (3)$$

$$\text{strain } (\varepsilon) = \frac{\beta\ cos\theta}{4} \qquad (4)$$

$$\text{strain \% } (\varepsilon\ \%) = \frac{\mathrm{a}-\mathrm{a}_0}{\mathrm{a}_0} \qquad (5)$$

$$\text{dislocation density } (\delta) = \frac{1}{D^2} \qquad (6)$$

$$\text{number of crystallites(N)} = \frac{t}{D^3} \qquad (7)$$

$$\mathrm{TC}_{(\mathrm{hkl})} = \frac{I\,(hkl)/\,I_0(hkl)}{\frac{1}{n}\Sigma I(hkl)/\,I_0(hkl)} \qquad (8)$$

Where, 'D' is crystallite size, 'a' is a measured lattice constant, 'a_0' is standard lattice constant '$I_{(hkl)}$' is measured relative intensity of a diffraction peak, '$I_{o\ (hkl)}$' is intensity of the standard powder diffraction peak, 'n' is the number of diffraction peaks.

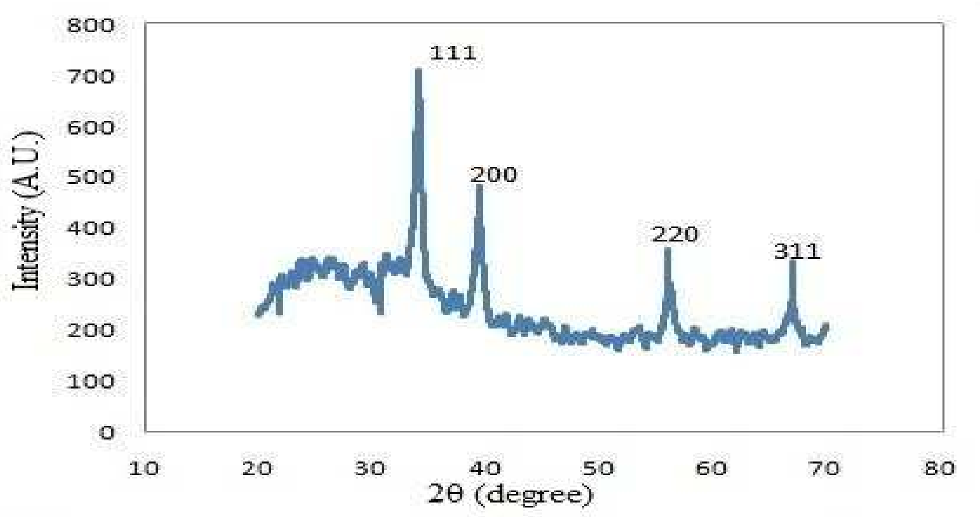


Figure 1. XRD pattern of CdO thin film .

If the texture coefficient of the film is one then crystallites in the sample are randomly oriented and if it is greater than one then there will be abundance of crystallite in given (hkl) direction. However if texture coefficient is less than one then it suggest lack of grains oriented in given direction. In present investigation the negative value of the strain (−0.033%) shows presence of compressive strain in CdO film. This very low value of compressive strain suggests that the synthesized CdO thin film exhibits high-quality crystal geometry. The various crystallographic parameters estimated are tabulated in table 1.

Table 1: Crystallographic and microstructural parameters of CdO thin film.

D(nm)	**a** (nm)	**ε**(Lin^{-2}nm)	**δ**(nm)$^{-2}$	**N**	**TC**	**ε %**
12.97	0.4538	2.79×10^{-3}	5.94×10^{3}	2.18×10^{26}	0.8646	-0.033%

Morphology

Fig. 2 shows SEM images of CdO thin film at two different magnifications grown by sol gel spin coating technique. The surface morphology of film shows cauliflower like nano structures grown on glass substrates. This structure makes film highly porous in nature.

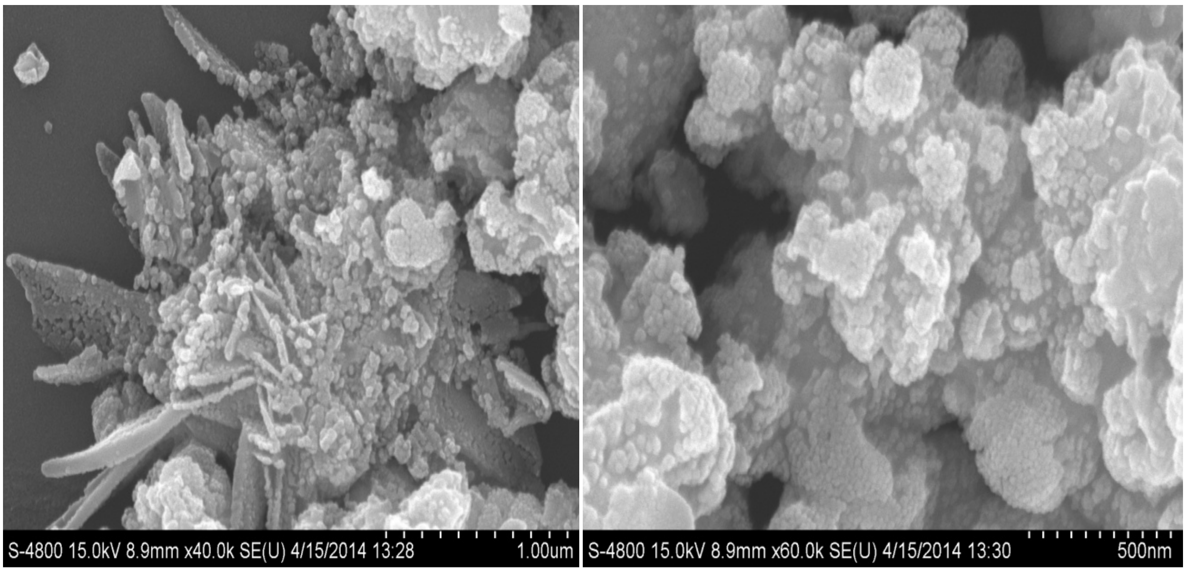


Figure 2. SEM images of CdO thin film at magnification ×40 k and ×60 k

Optical analysis

Optical properties of the as deposited CdO film were studied by analyzing UV-Vis transmission and absorption spectra taken in wavelength range 285 to 900 nm. The CdO film has low transmittance in UV region and it increase as wavelength approaches to visible region. The maximum value of transmittance for CdO thin film observed is 18 % which is in good agreement with the results reported by Mahdi.H.Suhail [2]. Conversely, it has high absorbance in UV region which decreases with increase in wavelength. The sharp decrease in absorption is observed near band edge .The pots of transmittance vs. wavelength and absorption vs. wavelength are shown in figure 3. The optical band gap of as deposited CdO thin film was determined by using tauc equation,

$$\alpha h\nu = A(h\nu - E_g)^n \tag{9}$$

Where α is absorption coefficient, $h\nu$ is photon energy, E_g is band gap energy, A and n are constants (n=1/2, 1/3, 2/3, 2).

The type of optical transition can be understood by plotting the plots of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{1/3}$, $(\alpha h\nu)^{2/3}$, $(\alpha h\nu)^2$ vs. photon energy hν. It was observed that the relation shows linear dependence for n=1/2 which conforms that deposited CdO material is direct band gap semiconductor. The optical band gap was determined by extrapolating the linear portion at α =0 on the photon energy axis (Fig. 4). The direct optical band gap of as-deposited CdO thin film was found to be 3.42 eV which is in good agreement with the value reported by Khallf [17].

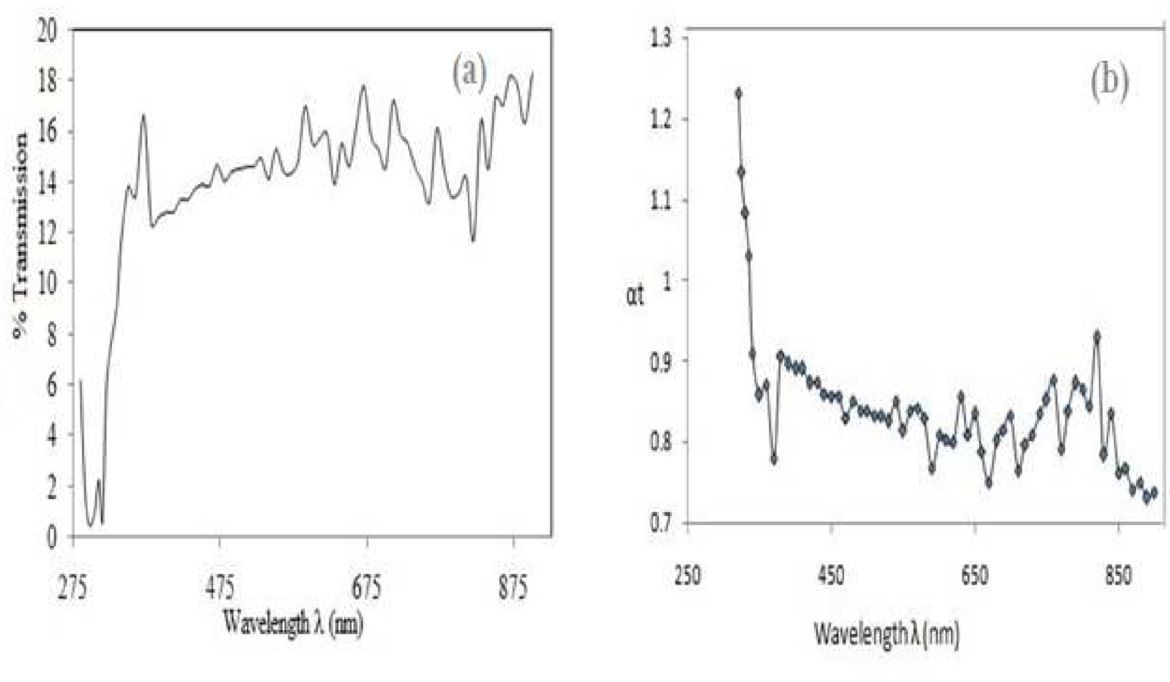


Figure 3. (a)Plot of % transmission Vs wavelength and (b) Plot of absorption vs. wavelength forCdO thin film.

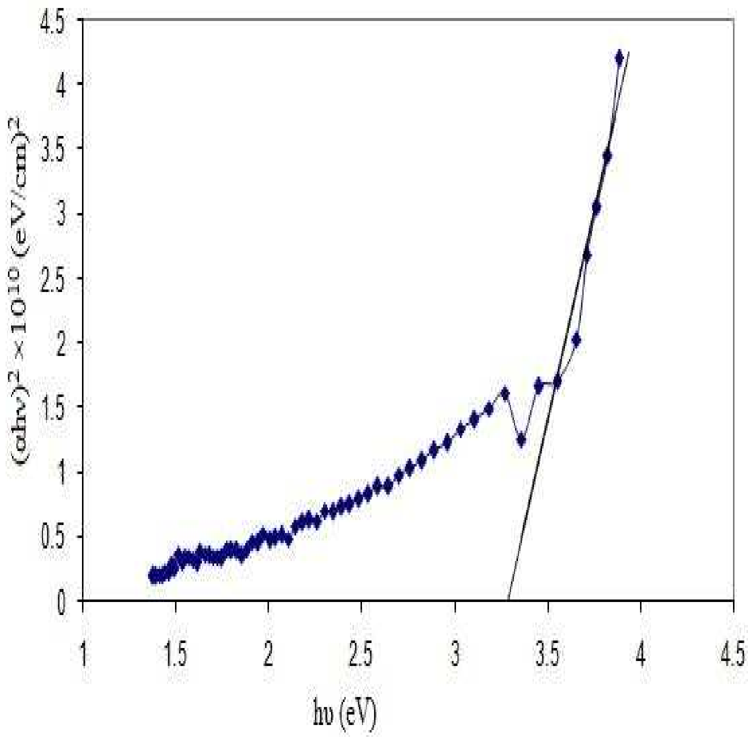


Figure 4. Plot of $(\alpha h\nu)^2 \times 10^{10}$ vs. Photon energy (hν)

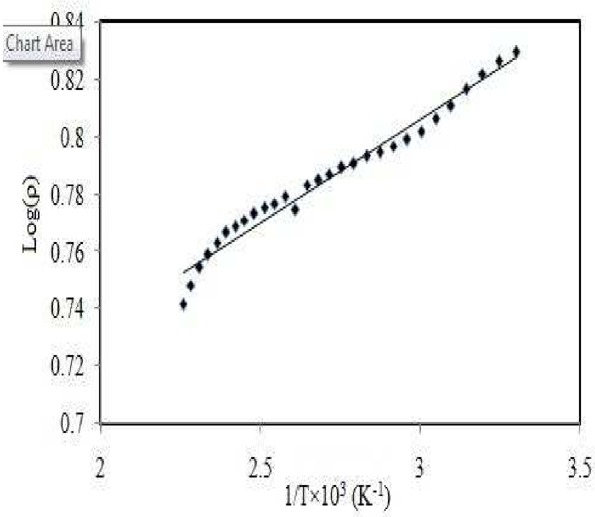
Electrical analysis

The dc electrical resistivity of as deposited CdO film was measured as a function of temperature in the temperature range 303 K to 443 K. The electrical resistivity of CdO film decreases with increase in temperature which indicates its semiconducting nature. Figure5 shows the variation of log(ρ) with reciprocal of temperature. The thermal activation energy of CdO film was calculated using relation,

$$\rho = \rho_0 e^{\frac{\Delta E}{KT}} \tag{10}$$

Where, T is the temperature, E is activation energy, K is Boltzmann's constant.

The activation energy of CdO thin film was found to be 0.019 eV.



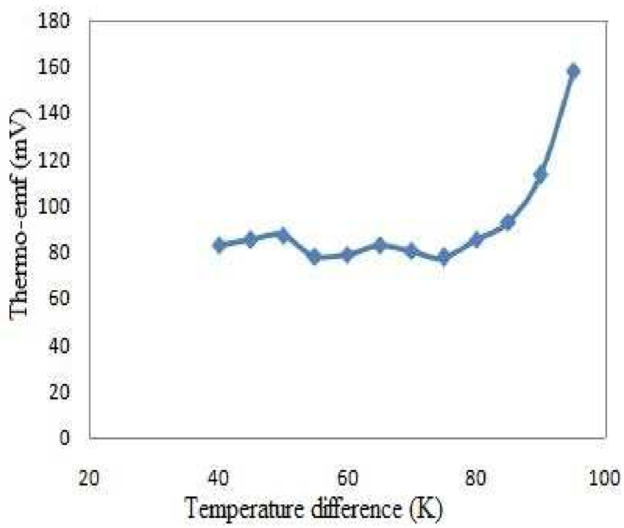


Figure 5 **Figure 6**

When temperature gradient is applied across a semiconductor thin film, then charge carrier transfer takes place from hot to cold end which gives thermal voltage. The thermo-emf generated across CdO thin film is proportional to the temperature difference across it (figure 6). The sign of thermo-emf generated gives the information of the dominant charge carriers inside the semiconductor. In the present investigation CdO films deposited by sol-gel spin coating technique are of n- type. The thermo-emf increases exponentially with applied temperature difference which may be because of increased charge carrier concentration and it's mobility.

CONCLUSION

The nanocrystalline transparent conducting CdO thin films were successfully deposited onto glass substrates by sol gel spin coating method. The CdO thin films are nanocrystalline in nature with cubic lattice. The SEM studies revealed that the CdO thin films are uniform, porous and well covered to the glass substrate. The optical absorption studies showed that CdO film exhibits 3.42 eV optical band gap. The electrical resistivity of CdO film is of the order of 10^{-5} Ωcm with n-type of conductivity.

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