ISSN : 0974 - 7524 Volume 9 Issue 4

Physical CHEMISTRY
An Indian Journal

Full Paper

PCAIJ, 9(4), 2014 [125-129]

Determination of optical dispersion parameters of sprayed CdO: MgO thin films

Ziad Abdulahad Toma

Al_Mustansiriyah University, College of Education, Physics Department/ Baghdad, (IRAQ)

E-mail : ziad_a_toma@yahoo.com

ABSTRACT

Sprayed CdO:6% Mg thin films have been grown on preheated glass substrates. The optical properties and dispersion parameters of the films have been studied as a function of heat treatment. The changes in dispersion parameters and Urbach tails were investigated. The optical energy gap Eg decreased with increasing annealing temperature to 450°C that increase the density of localized states and cause an expanding in the Urbach tail and consequently decrease the energy gap from 3.51 eV to 3.45 eV. The single-oscillator parameter has been reported.

KEYWORDS

TCOs;
Dispersion parameters;
CdO;
Spray pyrolysis.

INTRODUCTION

CdO is a well-known as transparent conductive oxide, which belongs to the wide-band-gap semiconductor family. It is a promising material for a variety of applications, and seems to be the most appropriate material for different applications in optoelectronic devices such as solar cells, optical filters, photovoltaic device, flat panel display, IR heat mirror, transparent electrodes, electrochromic devices, low-emissive windows, high stability thin film resistors, covering layers for fiber optical systems, photovoltaic devices[1-7]. Owing to their specific combined electrical, optical and chemical properties has dominated the present scientific world of thin films and gas sensing[8,9]. In addition, they exhibit low electrical resistivity and high optical transmittance.

Various techniques have been applied to study CdO films such as such as spray pyrolysis[10], chemical bath deposition (CBD)[11], chemical vapour deposition[12], reactive evaporation[13], DC magnetron sputtering[14], metal organic chemical vapor deposition (MOCVD)[15], and sol-gel method[16]. Among these methods, the spraying technique is a simple, economic and commonly used method and it is well suited for the preparation of tin dioxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings[17].

In addition, the CdO films prepared by the spraying technique are also physically and chemically resistant against environmental effects.

The current study investigates the optical dispersion characterization of CdO:6%Mg thin films prepared by spray pyrolysis technique. The optical properties of the films were examined in relationship to the heat treatment. The accurate determination of the optical properties of these films is important, not only in order to know the basic mechanisms underlying these phenomena, but also to exploit and develop their interesting technological applications.

EXPERIMENTAL PROCEDURE

Thin films of cadmium oxide have been prepared by spray pyrolysis technique. The starting solution was achieved by an aqueous solution of 0.1M $CdCl_2$ and $MgCl_2$ both from Sigma-Aldrich chemicals, this material was dissolved in de-ionized water and ethanol, a few drops of HCl were added to make the solution clear, formed the final spray solution and a total volume of 50 ml was used in each deposition. The spraying process was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 350°C, with the optimized conditions that concern the following parameters, spray time was 8 sec and the spray interval 3 min was kept constant to avoid excessive cooling, the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2}, distance between nozzle and substrate was about 29cm, solution flow rate 5 ml/min. Optical transmittance and absorbance were recorded in the wavelength range (300-900 nm) using UV-VIS spectrophotometer (Shimadzu Company Japan). In order to explore the influence of annealing temperature on the parameters under investigation, the as deposited films annealed to 400°C and 450°C.

RESULTS AND DISCUSSION

The optical properties of CdO:6%Mg films by means of optical absorption in the UV-VIS region (300–900) nm have been investigated. The absorption coefficient (α) could be calculated using the following relation[18]:

$$\alpha = \frac{2.303A}{t} \quad (1)$$

Where (A) is the absorption and (t) is the film thickness. Figure 1 shows the dependence of the absorption coefficient (α) on wavelength. The absorption coefficient slightly increases with the increasing of annealing temperature. In fact, increasing annealing temperature could induce a significant deformation of the crystalline state, which suggests modifications in the electronic structure[19]. As a result the decrease in the optical band gap with increasing film thickness can be attributed to the presence of unstructured defects that increase the density of localized states in the band gap and consequently decrease the energy gap such result was also obtained by Rusu et al.[20].

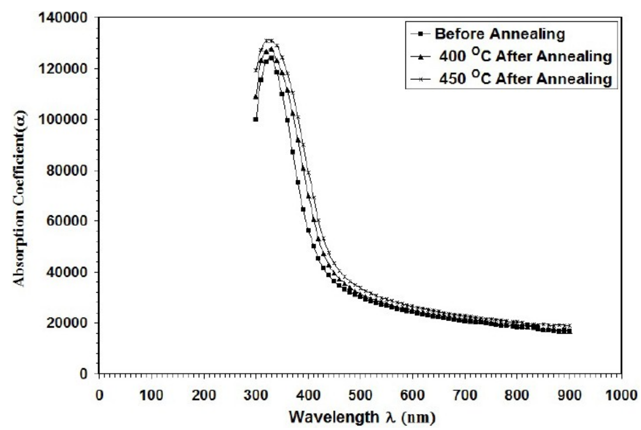

Figure 1 : Absorption coefficient versus wavelength for CdO:6%Mg films

The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach[21]. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as[22,23]:

$$\alpha = \alpha^\circ \exp (h\upsilon / E_U) \quad (2)$$

Where α° is a constant, E_U is the Urbach energy, which characterizes the slope of the exponential edge. Figure 2 shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of lnα vs. hυ and is given in TABLE 1. Increasing annealing temperature change the width of the localized states in the optical band. E_U values change inversely with the optical band gap. The Urbach energy values of the films were 769, 800, 833 meV for the as deposited, annealed films at 400 and 450ºC respectively. The increase of E_U suggests that the atomic structural disorder of the films increase after heat treatment. This behavior can result from increasing the concentration of point defects and formation of solid solution. So, this increase leads to a redistribution of states, from band to tail. As a result, both a decrease in the optical gap and expanding of the Urbach tail are taken place.

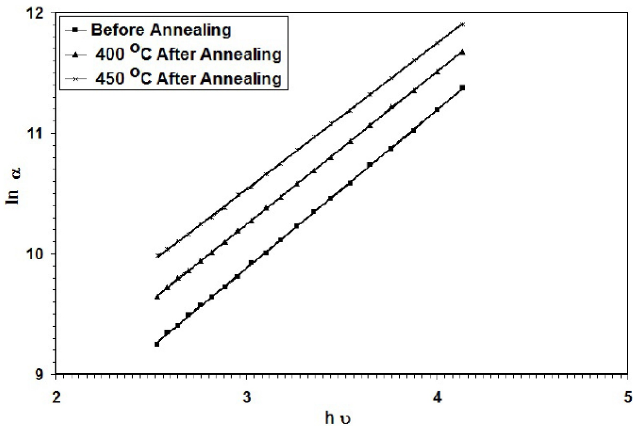

Figure 2 : lnα versus photon energy for CdO:6%Mg films

The dispersion parameters of the films were evaluated according to the single-effective-oscillator model using the following relation[24]:

$$n^2-1 = [E_d E_o / E_o^2 - E^2] \quad (3)$$

The physical meaning of the single-oscillator energy E_o is that it simulates all the electronic excitation involved and E_d is the dispersion energy related to the average strength of the optical transitions[25], which is a measure of the intensity of the inter band optical. This model describes the dielectric response for transitions below the optical gap. $(n^2-1)^{-1}$ vs. $(h\upsilon)^2$ plots for the films was plotted as shown in Figure 3. E_o and E_d values were determined from the slope, $(E_oE_d)^{-1}$ and intercept (E_o/E_d), on the vertical axis and are given in TABLE 1. E_o values decreased as the optical band gap decreases. According to the single-oscillator model, the single oscillator parameters E_o and E_d are related to the imaginary part of the complex dielectric constant, the moments of the imaginary part of the optical spectrum M_{-1} and M_{-3} moments can be derived from the following relations[26]:

$$E_o^2 = M_{-1} / M_{-3} \quad (4)$$

$$E_d^2 = M^3_{-1} / M_{-3} \quad (5)$$

The values obtained for the dispersion parameters E_o, E_d, M_{-1} and M_{-3} are listed in TABLE 1. The obtained M_{-1} and M_{-3} moments changes with annealing, the results show that both M_{-1} and M_{-3} are increased with increasing the annealing temperature.

For the definition of the dependence of the refractive index (n) on the light wavelength (λ), the single-term Sellmeier relation can be used[27]:

$$n^2(\lambda) - 1 = S_o\lambda_o^2 / 1 - (\lambda_o/\lambda)^2 \quad (6)$$

Where λ_o is the average oscillator position and S_o is the average oscillator strength. The parameters S_o and λ_o

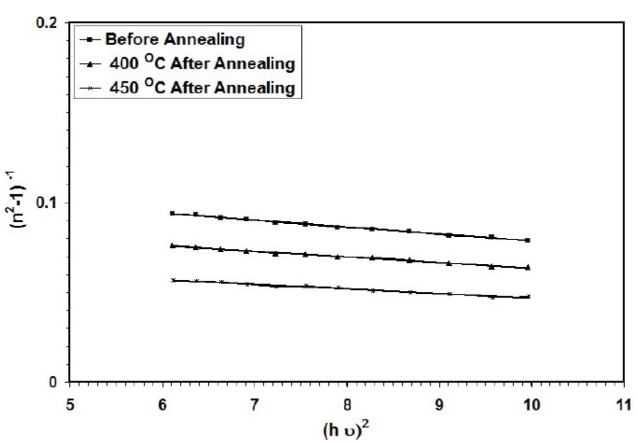

Figure 3 : Variation in $(n^2 - 1)^{-1}$ as a function of $(h\upsilon)^2$ for CdO:6%Mg films

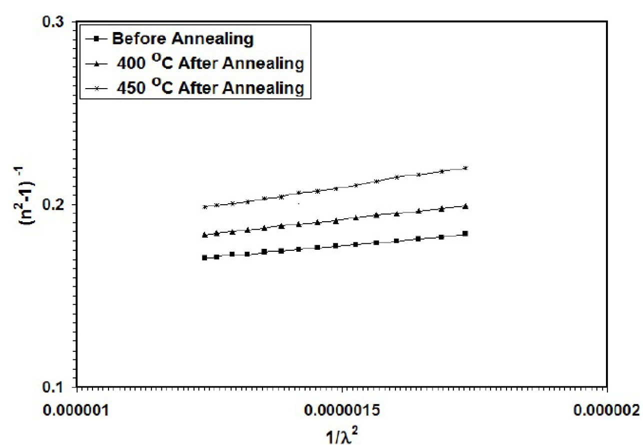

Figure 4 : Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for CdO:6%Mg films

TABLE 1 : The optical parameters

Sample	E_o (eV)	E_d (eV)	E_g (eV)	E_u meV	ε_∞	n(o)	M_{-1} eV^{-2}	M_{-3} eV^{-2}	S_o x10^{13} m^{-2}	λ_o nm
As deposited	5.03	50.32	2.51	769	11	3.32	10	0.395	3.87	414
Annealed at 400°C	4.96	62.11	2.48	800	13.5	3.67	12.5	0.506	3.03	445
Annealed at 450°C	4.89	81.64	2.45	833	17.6	4.2	16.67	0.694	2.24	494

Full Paper

in Eq. (6) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ against λ^{-2} as shown in Figure 4, the slope of the resulting straight line gives $1/S_o$, and the infinite-wavelength intercept gives $1/S_o\lambda_o^2$. The results shows a decrease in the band gap which may be attributed to the presence of unstructured defects, that increase the density of localized states and cause an expanding in the Urbach tail and consequently decrease the energy gap.

The optical conductivity was calculated using the relation[28]:

$$\sigma = \alpha n c / 4\pi \quad (7)$$

Where (c) is the velocity of light.

Figure 5 shows the variation of optical conductivity with the wavelength. It was observed that the optical conductivity increases with the increasing of annealing temperature to 450ºC. It can be notice from the figure that the optical conductivity for all films increased in the high photon energies region and decreased in the low photon energy region, this decrease is due to the low absorbance of the films in that region.

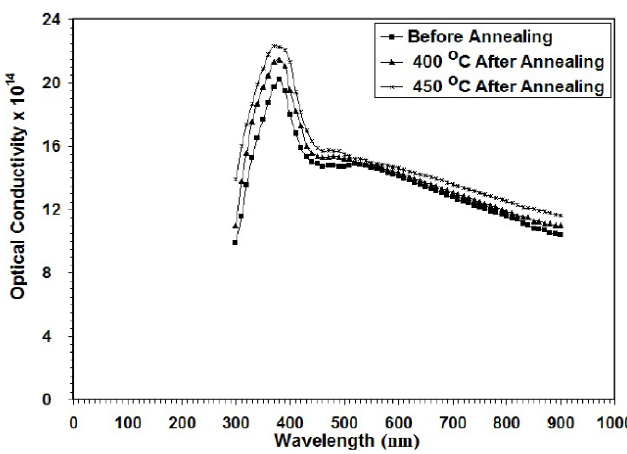

Figure 5 : Optical conductivity versus wavelength for CdO:6%Mg films

CONCLUSION

Sprayed CdO:6%Mg films were prepared on pre-heated glass substrates. The optical dispersion parameters were characterized and studied as a function of annealing. Optical band gap decreased with increasing annealing temperature. The single–oscillator parameters were determined. It was shown that the dispersion parameters of the films obeyed the single oscillator model, the change in dispersion was investigated and its value decreased from 5.3 to 4.89 with increasing annealing temperature to 450ºC.

REFERENCES

[1] V.Eskizeybek, A.Avcı, M.Chhowalla; Structural and optical properties of CdO nanowires synthesized from $Cd(OH)_2$ precursors by calcinations, Cryst.Res.Technol., **46**, 1093-1100 **(2011)**.

[2] Guillermo Santana, Arturo Morales-Acevedo, Osvaldo Vigil, Lidice Vaillant, Francisco Cruz, Gerardo Contreras-Puente; Structural and optical properties of $(ZnO)_x(CdO)_{1-x}$ thin films obtained by spray pyrolysis, Thin Solid Films, **373**, 235-238 **(2000)**.

[3] Wenting Dong, Congshan Zhu; Optical properties of surface-modified CdO nanoparticles, Optical Materials, **22**, 227-233 **(2003)**.

[4] L.M.Su, N.Grote, F.Schmitt; Diffused planar InP bipolar transistor with a cadmium oxide ûlm emitter, Electron.Lett., **20**, 716-717 **(1984)**.

[5] R.Kondo, H.Okhimura, Y.Sakai; Electrical properties of Semiconductor Photodiodes with Semitransparent films, Jpn.J.Appl.Phys., **10**, 176 **(1971)**.

[6] C.H.Champness, K.Ghoneim, J.K.Chen; An improved conventional Se–CdO photovoltaic cell, Canadian Journal of Physics, **63(3)**, 767-771 **(1985)**.

[7] S.Ilican, M.Caglar, Y.Caglar, F.Yakuphanoglua; CdO:Al films deposited by sol–gel process: A study on their structural and optical properties, Optoelectronics and Advanced Materials-RAPID communications, **3(2)**, 135-140 **(2009)**.

[8] K.T.Ramakrishna Reddy, G.M.Shanthini, D.Johnston, R.W.Miles; Highly transparent and conducting CdO films grown by chemical spray pyrolysis, Thin Solid Films, **427**, 397-400 **(2003)**.

[9] R.L.Mishra, A.K.Sharmaa, S.G.Prakash; Gas sensitivity and characterization of cadmium oxide (CdO) semi conducting thin film deposited by spray pyrolysis technique, Digest Journal of Nanomaterials and Biostructures, **4(3)**, 511-518 **(2009)**.

[10] Osvaldo Vigil, Francisco Cruz, Arturo Morales-Acevedo, Gerardo Contreras-Puente, L.Vaillant, G.Santana; Structural and optical properties of annealed CdO thin films prepared by spray pyrolysis, Material Chemistry and Physics, **68**, 249-252 **(2001)**.

[11] K.Gurumurugan, D.Mangalraj, S.K.Narayandas,

C.Balasubramanian; Phys.Status Solidi (a), **143**, 85 **(1994)**.

[12] Hani Khallaf, Chia-Ta Chen, Liann-Be Chang, Oleg Lupan, Aniruddha Dutta, Helge Heinrich A.Shenouda, Lee Chow; Investigation of chemical bath deposition of CdO thin films using three differentcomplexing agents. Applied Surface Science, **257**, 9237-9242 **(2011)**.

[13] W.S.Lau, S.J.Fonach; J.Electron.Mater., **16**, 3 **(1987)**.

[14] T.K.Subramanyam, B.Srinivasulu Naidu, S.Uthanna; Studies on dc magnetron sputtered cadmium oxide films. Applied Surface Science, **169(170)**, 529-534 **(2001)**.

[15] R.S.Mane, H.M.Pathan, C.D.Lokhande; Sung-Hwan Han, An effective use of nanocrystalline CdO thin films in dye-sensitized solar cells, Solar Energy, **80**, 185-190 **(2006)**.

[16] S.Sakthivel, D.Mangalaraj; Cadmium Oxide Nano Particles by Sol-Gel and Vapour-Liquid-Solid Methods, Nano Vision, **1(1)**, 47-53 **(2011)**.

[17] Pramod S.Patil; Versatility of chemical spray pyrolysis technique, Materials Chemistry and Physics, **59**, 185–198 **(1999)**.

[18] X.Han, R.Liu, W.Chen, Z.Xu; Properties of nanocrystalline zinc oxide thin films prepared by thermal decomposition of electrodeposited zinc peroxide, Thin Solid Films, **516**, 4025-4029 **(2008)**.

[19] Zheng Biju, Hu Wen; Influence of substrate temperature on the structural and properties of In-doped CdO films prepared by PLD, Journal of Semiconductors, **34(5)**, 053003-1- 053003-6 **(2013)**.

[20] R.S.Rusu, G.I.Rusu; On The Electrical and Optical Characteristics of CdO Thin Films, Journal of Optoelectronics and Advanced Materials, **7(3)**, 1511-1516 **(2005)**.

[21] F.Urbach; The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids, Phys.Rev., **92**, 1324-1325 **(1953)**.

[22] J.Tauc; Amorphous and Liquid Semiconductors, Plenum Press, New York, **(1974)**.

[23] J.Tauc, R.Grigorovici, A.Vancu; Optical Properties and Electronic Structure of Amorphous Germanium, Phys.Status Solidi, **15**, 627-637 **(1966)**.

[24] S.H.Wemple, DiDomenico; Behavior of the Electronic Dielectric Constant in Covalent and Ionic Materials, Phys.Rev.B3, 1338-1351 **(1971)**.

[25] S.H.Wemple; Refractive-index behavior of amorphous semiconductors and glasses, Phys.Rev.B7, 3767-3777 **(1973)**.

[26] H.E.Atyia; Influence of deposition temperature on the structural and optical properties of InSbSe3 films, Optoelectron.Adv.M., **8**, 1359-1366 **(2006)**.

[27] S.H.Wemple, DiDomenico; Oxygen – Octahedra Ferroelectrics I. Theory of Electro-Optical and Non Linear Optical Effects, J.Appl.Phys., **40(2)**, 720-734 **(1969)**.

[28] J.I.Pankove; Optical processes in semiconductors, Dover Publications, Inc. New York, **91**, **(1975)**.