

The Effect of Composition Ratios on Structural and Optical Properties of $(\text{ZnO})_{1-x}(\text{CdO})_x$ Thin Films Prepared by PLD.

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Abstract— In this work $(\text{ZnO})_{1-x}(\text{CdO})_x$ films were prepared by using Pulse laser deposition. Annealing in air at temperature 500 °C at constant time of 180 min. The crystalline structure was studied by X-ray diffraction (XRD) having found the presence of the ZnO hexagonal at $X=0$ and cubic phase pattern for CdO at $x=1$ and a mixing of cubic-CdO and hexagonal-ZnO phases for ($X= 0.3, 0.4$ and 0.5) concentrations. The crystallinity of all samples improves with the thermal annealing. The optical band-gap was also studied from the optical transmittance for the as grown and annealed samples. As expected, the band-gap changes between that for pure CdO and that for ZnO.

Index Terms— $(\text{ZnO})_{1-x}(\text{CdO})_x$ films ,PLD,optical and structural properties of $(\text{ZnO})_{1-x}(\text{CdO})_x$ films ,annealing,

1 INTRODUCTION

Transparent conducting oxides (TCOs) have been extensively studied because of their applications in semiconductor optoelectronic device technology.

Some of these transparent metallic oxides include, in part zinc oxide (ZnO), indium-tin oxide (ITO), tin oxide (SnO_2) and cadmium oxide (CdO). CdO and ZnO are both promising material for their application as window and buffer layers in thin film solar cell. CdO is an n-type semiconductor, with a direct band gap of approximately 2.5 eV[1] which is lower than that of ZnO(3.3eV)[2]. It is known that it is difficult to obtain simultaneously a high transmission in the visible region and good conductivity qualities [3]; however, a ternary compound which combines these properties in a controlled way may allow the optimization of the window layer on the solar cell. Since Zn and Cd belong to the same group in the periodic table, it is fundamental and practical interest to study the Cd-Zn-O ternary system cadmium zinc oxide (CdO-ZnO), the ternary TCO material, is a transparent conductor material that combines many beneficial characteristics of both CdO and ZnO. The ratio of Cd and Zn actions becomes important for obtaining a TCO film [4].

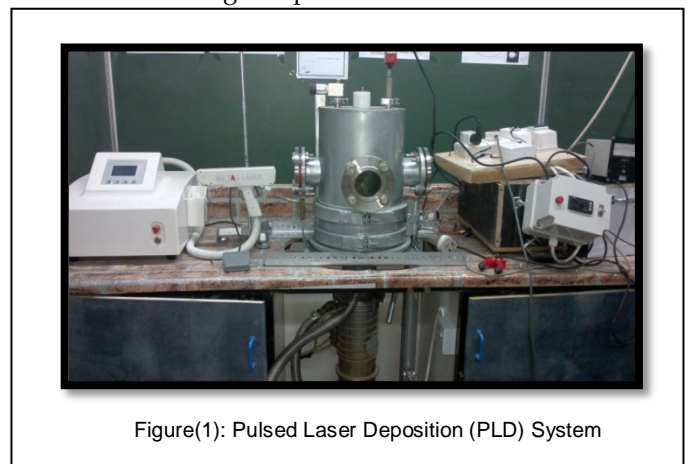
CdO thin films are prepared by various physical and chemical deposition techniques such as pulsed laser deposition[5,6], magnetron sputtering [7,8], RF sputtering [9], sol-gel[10,11], spray pyrolysis [12,13], chemical bath deposition [14], metal organic chemical vapor deposition(MOCVD)[15],

2 EXPERIMENTAL METHODS

The deposition of $(\text{ZnO})_{1-x}(\text{CdO})_x$ film was performed in a vacuum chamber. The chamber was evacuated using a diffusion pump to a base pressure of 4×10^{-5} mbar and then filled with oxygen (99.99% purity) at a working pressure of 4×10^{-2} mbar. $(\text{ZnO})_{1-x}(\text{CdO})_x$ target with $x = 0, 0.3, 0.4, 0.5$ and 1. was ablated by a Nd:YAG pulsed laser with a wavelength of 1064 nm, pulse duration of 10 ns and frequency of 6 Hz. Low energy fluency was set at 500mj /cm² as shown in figure (1). $(\text{ZnO})_{1-x}(\text{CdO})_x$ films were grown on glass substrates. The target-substrate distance was kept at 2cm. The deposition time of 3 min was maintained. The $(\text{ZnO})_{1-x}(\text{CdO})_x$ thin films were deposited at room temperature. After deposition, film crystal structure was investigated by an X-ray diffraction apparatus with $\text{Cu K}\alpha$ incident radiation was used to identify the phase structure of the grown films. The optical properties of the $(\text{ZnO})_{1-x}(\text{CdO})_x$ thin films were characterized by UV-vis spectrophotometer. All spectra were measured at annealing temperature 500 C.

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and electrode position[16-17].

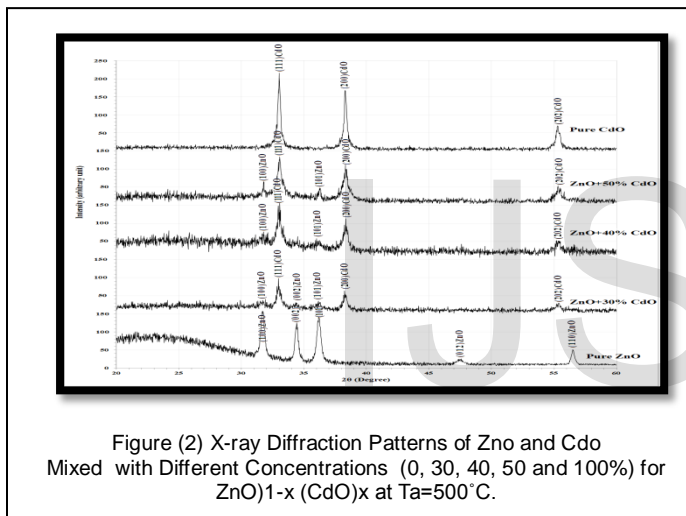


Figure(1): Pulsed Laser Deposition (PLD) System

3 RESULTS AND DISCUSSION

3.1 Structural properties of ZnO films

Figure (2) shows the x-ray diffraction (XRD) patterns of the $(\text{ZnO})_{1-x}(\text{CdO})_x$ composite films with different CdO contents at 500°C. For the composite films with 0 at. % CdO, the peaks of CdO cannot be clearly detected due to the small fraction of CdO. However, the peaks of ZnO(100)(002)(101) planes can be clearly seen for the film with 0 at.% CdO, while, the peaks of CdO(202)(200)(111) planes can be clearly seen for the film with 30 at.% CdO, and the peak intensity of CdO increases with the increasing CdO content in the composite. It is also seen that as the content of CdO increases, the peak of ZnO (101)(002)(100)(101)(002)(100) decreases, where the composite films with 40 and 50 at.% CdO, the peaks (002) of ZnO cannot be clearly seen. However, for the composite films with 100 at.% CdO, the peaks of ZnO cannot be clearly detected due to the small fraction of ZnO. Our results are in agreement with Afif Fouzri et al. [18]



resulting in the red shift of absorption edge. One is that the increase of crystalline size can cause red shift of absorption edge. The other is that the part phase transforms from anatase to rutile leads to the decrease of band gap [19]

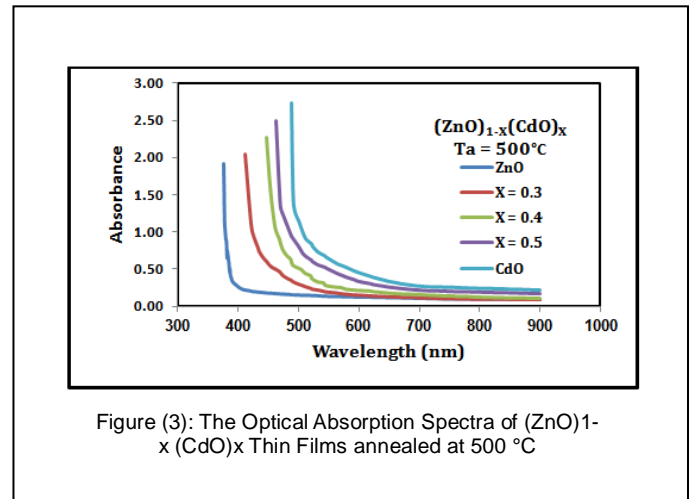


Figure (3): The Optical Absorption Spectra of $(\text{ZnO})_{1-x}(\text{CdO})_x$ Thin Films annealed at 500 °C

3.2.2 Optical Energy Gap

The optical energy gap values (E_g^{opt}) for $(\text{ZnO})_{1-x}(\text{CdO})_x$ films have been determined by plotting the relation of $[(\alpha h\nu)^2]$ versus $h\nu$ (eV) for direct energy gap as shown in figure (4). The figure shows the E_g of ZnCdO films deposited on glass substrate at different concentrations ($x=0,0.3,0.4,0.5,1$) of $(\text{ZnO})_{1-x}(\text{CdO})_x$ for annealing temperature (RT,300,500). The concentration films exhibited a reduction in the energy optical gap, it is decreased from 3.3 eV at 375 nm of ZnO to 2.2eV at 563 nm of CdO. The shift of optical energy can be explained in terms of quantum-size effect in which the film with large crystallites [91], thus resulting in an improvement in crystalline of $(\text{ZnO})_{1-x}(\text{CdO})_x$ films and so the density of localized states decreases. This is in a good agreement with the experimental results of XRD analysis which means that the optical quality of $(\text{ZnO})_{1-x}(\text{CdO})_x$ films is improved by annealing our results are in agreement with Singh et al. [20].

3.2 Optical properties of $(\text{ZnO})_{1-x}(\text{CdO})_x$ films

The optical properties of the $(\text{ZnO})_{1-x}(\text{CdO})_x$ films deposited by pulsed laser deposition technique are measured by UV-VIS spectrophotometer on glass substrate of various concentrations ($X=0,0.3,0.4,0.5,1$) of $(\text{ZnO})_{1-x}(\text{CdO})_x$. The laser fluence energy density is 0.5 J/cm² and the oxygen pressure is maintained at 10⁻² mbar at annealing temperature 500 °C with film average thickness 200 nm. The absorption and transmittance have been studied.

3.2.1 The Optical Spectrum (A)

The optical absorbance of $(\text{ZnO})_{1-x}(\text{CdO})_x$ films depends on the concentration as shown in figure (3) at different concentrations (0,0.3,0.4,0.5,1) of $(\text{ZnO})_{1-x}(\text{CdO})_x$ for annealing temperature 500 C. Further observation shows that the absorbance of the $(\text{ZnO})_{1-x}(\text{CdO})_x$ films increases with increasing of concentration. This is probably ascribed to the increase of particle sizes and surface roughness. Furthermore, the absorption edges of the $(\text{ZnO})_{1-x}(\text{CdO})_x$ films have a small red shift with increasing of concentration. There are two possible factors

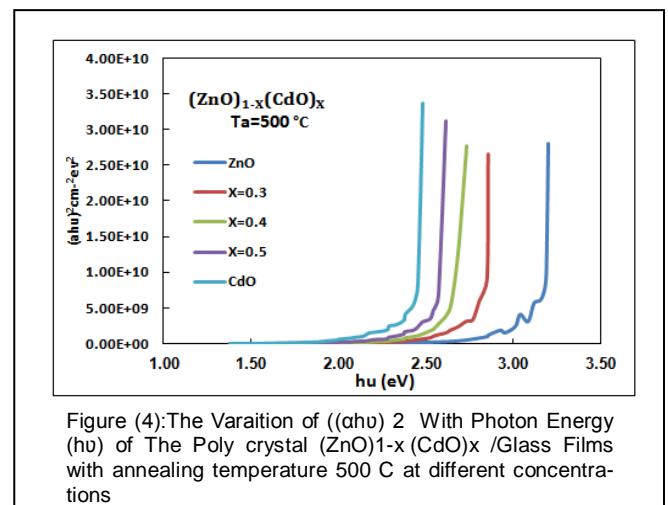


Figure (4): The Variation of $(\alpha h\nu)^2$ With Photon Energy ($h\nu$) of The Poly crystal $(\text{ZnO})_{1-x}(\text{CdO})_x$ /Glass Films with annealing temperature 500 C at different concentrations

3.2.3 Refractive Index (n)

Figure (5) shows the variation in refractive index with wavelength for $(\text{ZnO})_{1-x}(\text{CdO})_x$ film in the wavelength range of (300-900) nm for annealing temperature 500C and for different concentrations ($x=0,0.3,0.4,0.5,1$) of $(\text{ZnO})_{1-x}(\text{CdO})_x$. It is observed that the refractive index, in general, decreases slightly with increases of concentration. The refractive of perovskite thin film is known to proportional to distance between atomic planes. This result can be explained by a decrease in the density of the film due to better packing and decreased crystalline

mined through using equations ($\epsilon_r = n^2 - k^2$) and ($\epsilon_i = 2n k$), respectively. The plot of real and imaginary (ϵ_r, ϵ_i) parts of the Dielectric constant with wavelength for $(\text{ZnO})_{1-x}(\text{CdO})_x$ deposited for annealing temperature 500 C with different concentrations ($x=0.0.3,0.4,0.5,1$) of $(\text{ZnO})_{1-x}(\text{CdO})_x$ as shown in figures (7) and (8), respectively. It depends mainly on the extinction coefficient values according to the relationship between them. The real part of the dielectric constant decreases and the imaginary part increases with increasing concentrations.

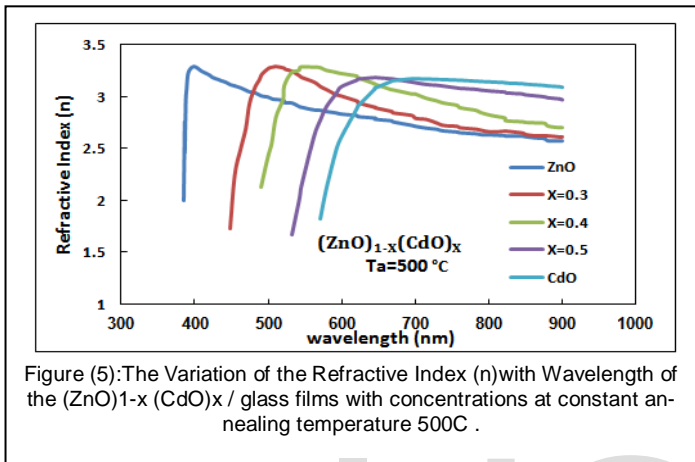


Figure (5): The Variation of the Refractive Index (n) with Wavelength of the $(\text{ZnO})_{1-x}(\text{CdO})_x$ / glass films with concentrations at constant annealing temperature 500C .

3.2.4 Extinction Coefficient (K)

The relation between the extinction coefficient and wavelength for $(\text{ZnO})_{1-x}(\text{CdO})_x$ films deposited at annealing temperatures 500 C as shown in Figure (6). From this figure, we can see that the extinction coefficient (k) takes the similar behavior of the corresponding absorption. This is attributed to the same reason mentioned previously in the absorption. We can observe from this figure (6) that extinction coefficient increases with increases concentrations ratio.

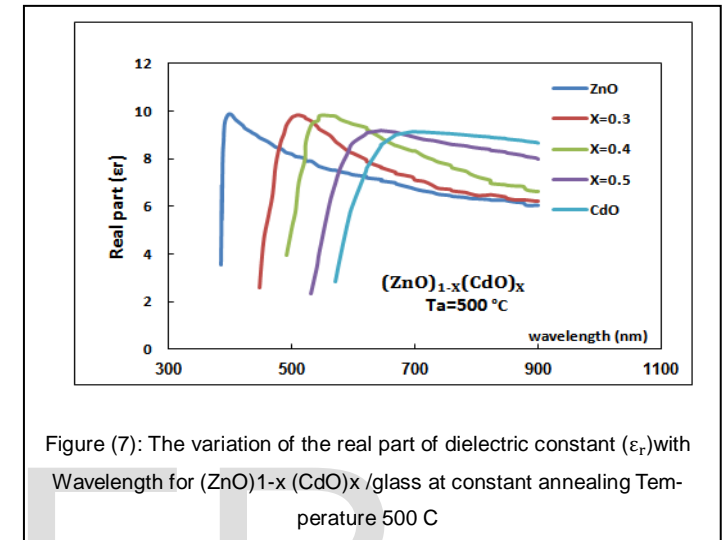


Figure (7): The variation of the real part of dielectric constant (ϵ_r) with Wavelength for $(\text{ZnO})_{1-x}(\text{CdO})_x$ /glass at constant annealing Temperature 500 C

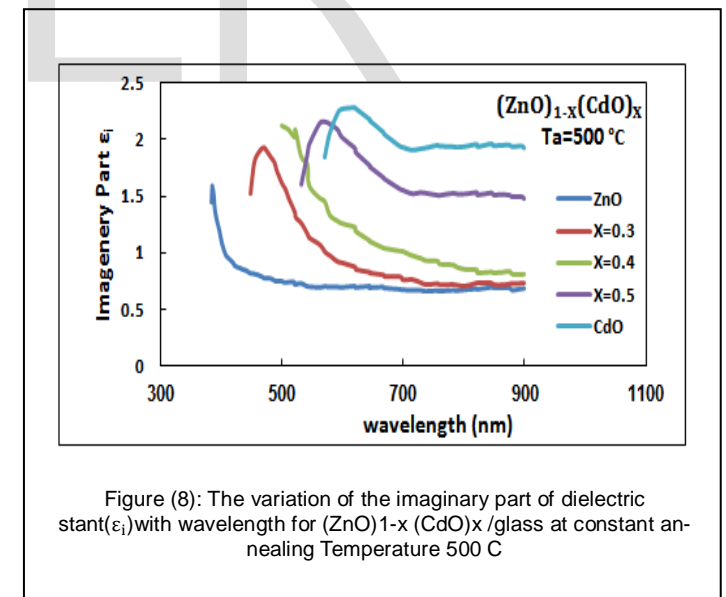


Figure (8): The variation of the imaginary part of dielectric constant (ϵ_i) with wavelength for $(\text{ZnO})_{1-x}(\text{CdO})_x$ /glass at constant annealing Temperature 500 C

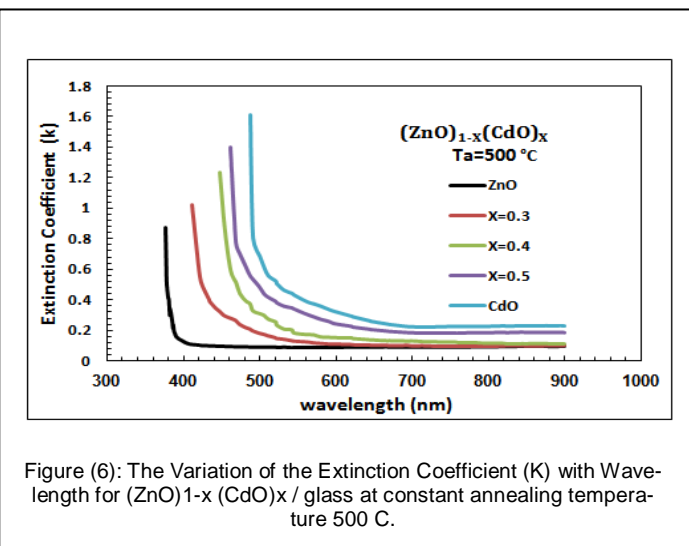


Figure (6): The Variation of the Extinction Coefficient (K) with Wavelength for $(\text{ZnO})_{1-x}(\text{CdO})_x$ / glass at constant annealing temperature 500 C.

3.2.5 Dielectric Constant (ϵ_r, ϵ_i)

Real and imaginary parts of dielectric constant are deter-

4. Conclusions

Structural and optical analysis show that pulse laser deposition technique is a useful method for the deposition of $(\text{ZnO})_{1-x}(\text{CdO})_x$ thin films.

For x (0,0.3,0.4,0.5 and 1) a mixing phase corresponding to cubic-CdO and hexagonal-ZnO is formed. Changes in the ab-

sorption spectra and on the corresponding values of the band-gap energy are correlated with the intermixing of transparent ZnO crystallites in-between CdO crystallites. The band-gap energy of pure CdO and pure ZnO reach the reported bulk values at room temperature. Usually a wide variety of band-gap values are reported in the literature for these semiconductor compounds. The band-gap change from 2.2 to 3.3 eV when the nominal composition x is changed from $x = 0$ to $x = 1$, respectively, for the annealed samples. The band-gap for each composition is also changed by the post-thermal annealing. The structural change affects the optical properties of the films.

REFERENCES

- [1] B.Saha, R. Thapa, K.K. Chattopadhyay, *Solid State Commun.* 145 (2008)33.
- [2] H. Guo, J. Zhou, Z. Lin, *Electrochim. Acta* 53 (2008) 146
- [3] K. I. Chopra, S. Major, D. K. Pandya, *Thin Solid Films* 102 (1983) 1.
- [4] A. Abdoladeh Ziabari, F. E. Ghodsi, "optoelectronic studies of sol-gel derived nanostructure CdO-ZnO composite films" *Journal of Alloys and Compounds* 509(2011) 8748-8755.
- [5] B.G. Lewis, D.C. Paine, *Mater. Res. Soc. Bull.* 25 (2000) 22-27.
- [6] K. Kawamura, K. Maekawa, H. Yanagi, M. Hirano, H. Hosono, *Thin Solid Films* 445 (2003) 182-185.
- [7] T.K. Subramanian, B.S. Naidu, S. Uthanna, *Appl. Surf. Sci.* 169 (2001) 529-534.
- [8] D. Ma, Z. Ye, L. Wang, J. Huang, B. Zhao, *Mater. Lett.* 58 (2003) 128-131.
- [9] N. Ueda, H. Maeda, H. Hosono, H. Kawazoe, *J. Appl. Phys.* 84 (1998) 6174-6177.
- [10] P.K. Gosh, S. Das, S. Kundoo, K.K. Chattopadhyay, *J. Sol-Gel Sci. Technol.* 34 (2005) 173-179.
- [11] R. Maity, K.K. Chattopadhyay, *Sol. Energy Mater. Sol. Cells* 90 (2006) 597-606.
- [12] K. Gurumurugan, D. Mangalaraj, S.K. Narayandass, K. Sekar, C.P.G. Valabhan, *Semicond. Sci. Technol.* 9 (1994) 1827-1832.
- [13] M. Kul, A.S. Aybek, E. Turan, M. Zor, S. Irmak, *Sol. Energy Mater. Sol. Cells* 91 (2007) 1927-1933.
- [14] A.J. Varkey, A.F. Fort, *Thin Solid Films* 239 (1994) 211-213.
- [15] Z. Zhao, D.L. Morel, C.S. Ferekides, *Thin Solid Films* 413 (2002) 203-211.
- [16] X. Han, R. Liu, Z. Xu, W. Chen, Y. Zheng, *Electrochim. Commun.* 7 (2005) 1195-1198.
- [17] H. Henriquez, P. Grez, E. Munoz, H. Gomez, J.A. Badan, R.E. Marotti, E.A. Dalchiele, *Thin Solid Films* 518 (2010) 1774-1778.
- [18] Afif Fouzri, Mohamed A. Boukadhaba, Al Housseynou Tauré, Nawfel S., Amor B., Vincent S., *Journal of Crystallization Process and Technology*, 3 (2013) 36-48
- [19] T. Supasai, S. Dangtip "Influence of Temperature Annealing on Optical Properties of SrTiO₃/BaTiO₃ Multilayered Films on Indium Tin Oxide" *J. Applied surface science*" Vol. 256, (2010), PP 4462-4467.
- [20] H. B. Sharma and Singh "Effect of crystallization on optical properties of sol-gel processed nano-sized strontium titanate (SrTiO₃) thin films" *J. Applied Physics*, Vol. 45, (2011), p133.