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Effect of Molar Concentration on the Optical and Structural Properties of CdO:In Thin Films Deposited by Spray Pyrolysis

¹Jinan Ali Abd, ²Rafia T. Ahmed, ³Nada A. Mohamed

^{1,2,3}Collage of Science for Women, Babylon University, Iraq.

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ABSTRACT

Cadmium oxide (CdO:2%In) thin films have been deposited onto glass substrates from different molar concentration of cadmium acetate precursor solution using a simple spray pyrolysis technique. The structural and optical properties of the films have been characterized by X-ray diffraction study and UV spectroscopy. The crystal structure of the deposited films were found to be polycrystalline of cubic structure with preferentially orientated along (111) crystallographic directions. Increase of molar concentration increases the films packing density and reorient the crystallites along (1 1 1) plane. There is an increase in the optical transmissions for all films with increasing in the wavelength and molar concentration. For different molar concentrations (0.1M, 0.2 M, and 0.3M), the direct band gap is found to be in the range (2.3, 2.35, and 2.45 eV). The band gap energies depend on molar concentration of solution.

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INTRODUCTION

Metal-doped degenerate semiconductor cadmium oxide (CdO) has been used extensively in transparent conducting oxide, solar cells (Trindade, T., *et al.*, 2001; Sravani, C., *et al.*, 1996) smart windows phototransistors (Su, L.M., *et al.*, 1984), diodes (Gomez Daza, O., *et al.*, 2001), transparent electrodes (Lewis, B.J. and D.C. Paine, 2000), and solid state gas sensors (Yan, M., *et al.*, 2001) and in many other optoelectronic applications. CdO thin films exhibit high transmission in the visible and UV regions, as well as a high ohmic conductivity. Bulk CdO shows n-type conductivity mainly due to oxygen vacancies. In the recent years, many different techniques such as thermal evaporation (Dakhel, A.A. and F.Z. Henari, 2003), sputtering (Subramanyam, T.K., *et al.*, 2001), solution growth (Varkey, A.J. and A.F. Fort, 1994), pulsed laser sputtering (Shagnov, I.I., *et al.*, 1981), activated reactive evaporation (Ramakrishna Reddy, K.T., *et al.*, 1998) and spray pyrolysis deposition (SPD) (Uplane, M.D., *et al.*, 2000; Murthy, L.C.S. and K.S.R.K. Rao, 1999; Kul, M., *et al.*, 2007), etc. have been used for the preparation of CdO thin film. SPD technique provides a simple route of synthesizing thin films because of its simplicity, low cost experimental setup from an economical point of view. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. This method has good control over the thickness uniformity and good adherence to the substrate. It was observed that with doping by different types of metallic ions, the physical properties of CdO could be controlled for optoelectronic applications. So that doping with ions like In, Sn, Al, Sc, and Y, improves its n-type conductivity and increases optical bandgap (Yan, M., *et al.*, 2001; Freeman, A.J., *et al.*, 2000; Ghosh, P.K., *et al.*, 2004; Lakshmanan, T.K. and J. Electrochem, 1963; Lakshmanan, T.K. and J. Electrochem, 1963; Dakhel, A.A., 2008). Surface roughnesses, in homogeneity and intrinsic defects, etc. are the cause of the optical losses. From the practical point of view, these properties can severely degrade or modify the performances of a component. Overall, the structural and optical properties of the thin films depend on the method of the preparation. The properties of the films are influenced by the geometry of the experimental setup. From industrial application point of interest, we have deposited CdO thin films and CdO:2%In under optimum conditions and studied their structural and optical properties more precisely for various molar concentrations of precursor solution by a locally developed SPD system, so as to reduce the preparation cost and make it economically more viable.

Experimental Details:

Spray pyrolysis deposition technique was used to prepare CdO and (0.1, 0.2, 0.3M) CdO:2%In thin films . CdO and (0.1M,0.2M 0.3 M) CdO:2%In thin films were prepared from solutions of cadmium acetate

Corresponding Author: Jinan Ali Abd, Collage of Science for Women, Babylon University, Iraq.
E-mail: jinanalit7077@yahoo.com

$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ diluted with methanol and distiller water in the ratio 1:1 and doping CdO solution in a ratio of (2%) with 0.1 M from mixture of InCl_3 and water distiller. The deposition of CdO:In thin films of different molar concentrations were carried by spraying an aqueous solutions onto a heated glass substrates at $(350 \pm 10^\circ\text{C})$. The optimized deposition parameters such as spray nozzle substrate distance (31cm), spray time (7s) and the spray interval (70s) were kept constant. The pressure of the carrier gas (N_2) was 4 mbar. The films thicknesses were measured by using Michelson Interferometer and found to be between (230-235nm). The crystalline structure of the films was confirmed by X-ray diffraction (XRD) with Cu $K\alpha$ radiation (Rigaku Model, $\lambda = 1.5406\text{\AA}$). The accelerating voltages of 40 kV, emission current of 30mA and the scanning speed of 5° per min were used. The transmittance and absorbance spectra for all films were recorded by (UV/VIS, Cecil, Cez200,7000 Series, Metertec).

RESULTS AND DISCUSSION

Structural Properties:

Figure 1 shows the X ray diffraction (XRD) patterns of the prepared CdO and CdO:2%In films of different molar concentrations (0.1,0.2,0.3M) respectively. All the patterns show polycrystalline of cubic CdO structure (NaCl structure) and CdO:In films are composed of crystallites of CdO (JCPDS Card No:05-0640) (Dakhel, A.A., 2010). XRD shows neither the formation of CdO_2 and In_2O_3 nor mixed phases even at In-doping level. It can be clearly seen that all films are preferentially orientated along (111) crystallographic directions and this is in agreement with the result obtained by others on film prepared by sputtering (Chu, T.L., S.S. Chu, 1903), vacuum evaporation (Dakhel, A.A. and F.Z. Henari, 2003) and spray pyrolysis (Uplane, M.D., *et al.*, 2000). And the preferential orientation peak for In doped films of different molar concentration became sharper and more intense. This may be attributed to the crystallinity of the CdO films being improved by increasing the molar concentration.

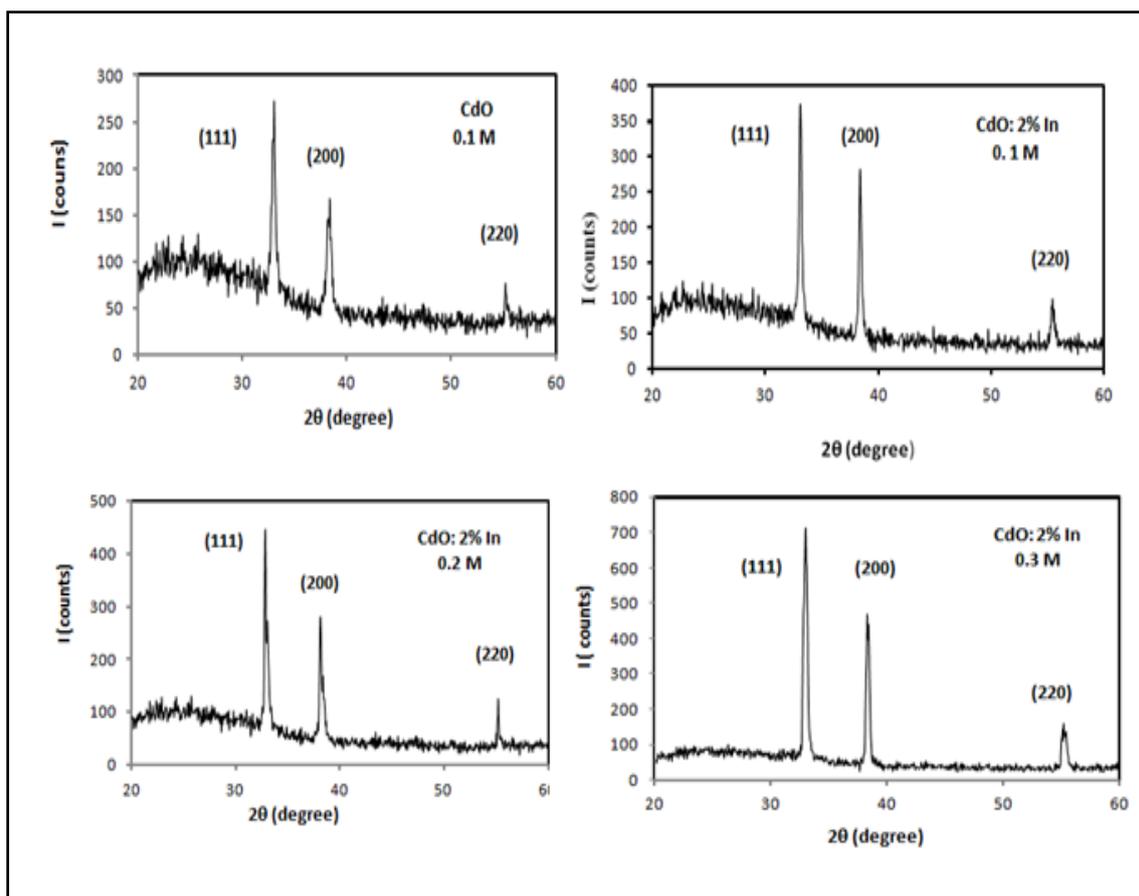


Fig. 1: The X ray diffraction (XRD) patterns of the prepared CdO and CdO:2%In films of different molar concentrations

Also, the structural parameters such as diffraction angle (2θ), lattice spacing (d), relative intensity of the peaks (I / I_0), full width at half maximum (FWHM), intensity (I) and the phases identified along (hkl) planes were evaluated from these spectra and presented in Table 1.

Table 1: The diffraction angle (2θ), interplaner distance (d), relative intensity of the peaks (I / I_0), (FWHM), intensity (I) and the phases identified along with (hkl) planes of CdO & CdO:In films

Material	2θ (deg)	D (Å)	I / I_0	FWHM (deg)	I (counts)	Identification with (hkl) values
CdO 0.1M	32.9696	2.71461	100	0.41410	114	(111) CdO
	38.2771	2.34952	62	0.53410	71	(200) CdO
	55.2581	1.66104	17	0.33570	19	(220) CdO
CdO:2%In 0.1M	33.0703	2.70657	100	0.25930	210	(111) CdO
	38.3662	2.34427	74	0.25580	156	(200) CdO
	55.3596	1.65824	20	0.22560	41	(220) CdO
CdO:2%In 0.2 M	32.816	2.70902	100	0.28380	232	(111) CdO
	38.1118	2.34528	61	0.31660	155	(200) CdO
	55.1427	1.66026	20	0.44580	40	(220) CdO
CdO:2%In 0.3 M	33.0396	2.72696	100	0.43000	239	(111) CdO
	38.3490	2.35933	66	0.34160	158	(200) CdO
	55.2864	1.66424	17	0.43330	41	(220) CdO

For all films, the grain size (D) was calculated from the full width at half maximum (FWHM) (β) of the preferred orientation diffraction peak by using the Scherrer equation (Rusu, D.I., *et al.*, 2011):

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

Where k denotes the Scherrer constant (the shape factor of the average crystallite and can be considered $k=0.90$, $\lambda=1.5406\text{Å}$ is the wavelength of the incident Cu $K\alpha$ radiation. From the results it may be said that nano-crystalline CdO material can be grown by our locally developed spray pyrolysis method. Larger D and smaller β values indicate better crystallization of the materials. According to Table 2, all CdO:2%In films of different molarities have better crystallinity levels as increasing in the molar concentration. Moreover the texture coefficient $TC(hkl)$ is introduced to characterize the preferential crystallite orientation along the (hkl) direction defined as (Saleem, M., *et al.*, 2012):

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N \sum I(hkl)/I_0(hkl)} \quad (2)$$

Where $I(hkl)$, $I_0(hkl)$ and N are the measured relative intensity of a diffraction peak, intensity of the standard powder diffraction peak and the number of diffraction peaks respectively. If $TC(hkl)=1$, for all the (hkl) planes considered, indicates a sample with randomly oriented crystallite, while values larger than 1, indicate the abundance of crystallite in a given (hkl) direction. Values $1 > TC(hkl) > 0$ indicate the lack of grains orientated in that direction. The TC values of the preferential crystallite orientation (111) of the all films were presented in Table 2. The calculated lattice constant (a) for the dominant peak of (1 1 1) of CdO and CdO:2%In of 0.2M are averaged to 4.7071Å and 4.6877Å respectively which are close to the reported value $a_0=4.695\text{Å}$ (Khan, M.K.R., *et al.*, 2010). Additionally, to have more information on the amount of defects in the films, the dislocation density (δ) was evaluated from the formula (Callister, W.D., *et al.*, 1997):

$$\delta = \frac{1}{D^2} \quad (3)$$

Where D is the grain size. This quantity, δ , is defined as the number of dislocations intersecting a unit area of a random section. It is seen from Table 2 that the δ value of all films is decreased with variation of molarities concentration. This means, increasing of molarities improves crystallite quality.

Table 2: FWHM (β), texture coefficient (TC), the grain size (D) and the dislocation density (δ) of the CdO and CdO:2%In films

Material	Molarities	Preferential Orientation	$\beta \times 10^{-3}$ (rad)	TC	D (nm)	$\delta \times 10^{-4}$ (nm^{-2})	a (Å)
CdO	0.1M	(111)	7.2237	1.43	19.2	27.1	4.7071
CdO:2%In	0.1M	(111)	4.5233	1.31	30.8	10.5	4.6877
CdO:2%In	0.2 M	(111)	4.9507	1.38	28.3	12.4	4.6920
CdO:2%In	0.3 M	(111)	7.5011	1.39	18.5	29.2	4.7232

Optical Properties:

Optical transmittance spectra of the CdO and CdO:2%In of different molarities films in the range of (400 - 900 nm) are presented in Figure 2, measured at room temperature in air. As seen in this figure, the optical transmissions of all films increased with increasing in the wavelength and the light transmission of CdO film increases as In doping and increasing in molar concentration. These spectra show that adding In to CdO with ratio of 2% and increasing the molarities improve the transmittance for all the deposited samples. The undoped films show a transmittance of 68% (550 nm) and the doping with increasing in molarities increase the transmittance value up to 84 % (550nm) for the 0.2M of CdO: 2%In. This effect of doping on the transmission of CdO films may be due to the structural and surface effects. These effects such as better crystallinity, less surface irregularity and defect density can increase the transmission.

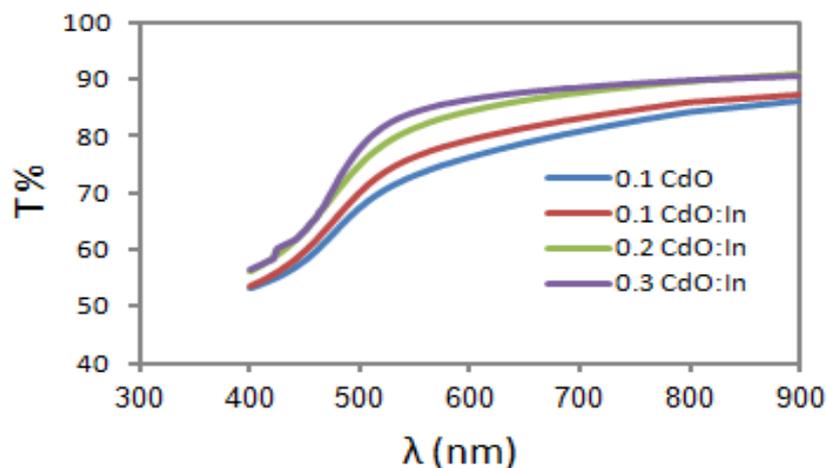


Fig. 2: Optical transmittance spectra of the CdO and CdO:2%In of different molarities films in the range of (400 - 900 nm)

The ability of a material to absorb light is measured by its absorption coefficient. Variation of optical absorption coefficient with wave length for various molar concentrations is shown in Figure 3. The absorption coefficient (α) is calculated from the transmittance spectrum using the relation (Miao, W., *et al.*, 2006):

$$\alpha = \ln(1/T) / t \quad (4)$$

Where T is the transmittance and t is the thickness of the film. Figure 4 shows the variation of absorbance spectra with the wavelength. It was clearly seen that the absorbance decreases with increasing in wavelength and molar concentration. The sharp increase in absorbance at the wavelength $\lambda \leq 550$ nm is due to the onset of interband transitions at the fundamental edge.

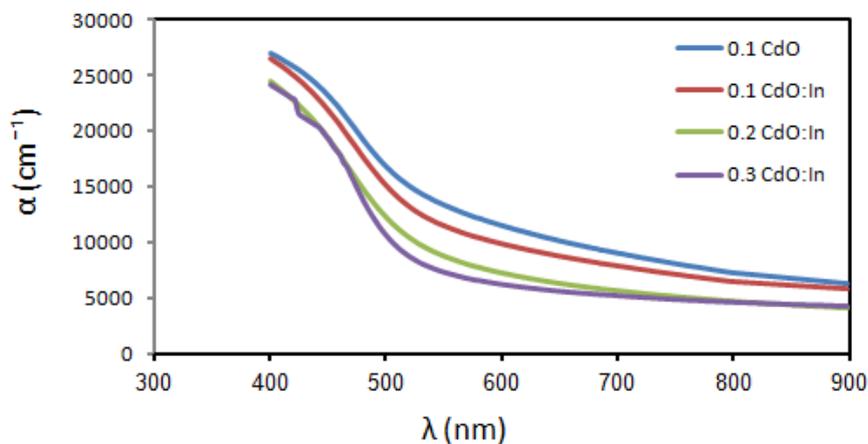


Fig. 3: Variation of optical absorption coefficient with wave length for various molar concentrations of CdO and CdO:2%In films

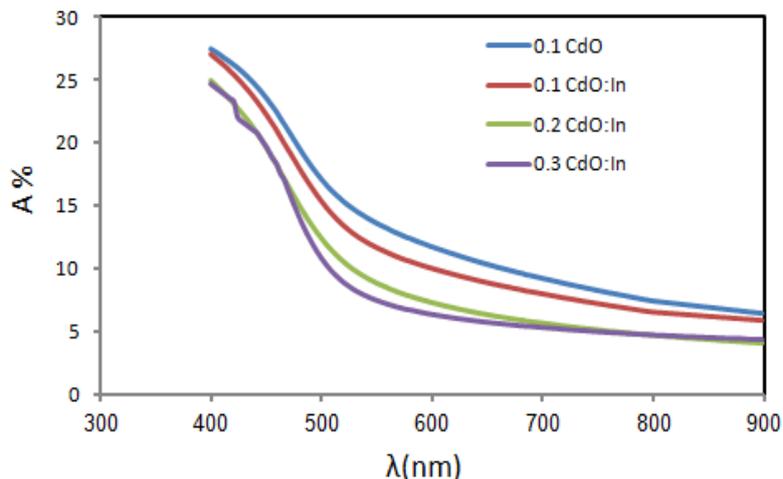


Fig. 4: Variation of absorbance spectra with the wavelength of various molar concentration for CdO and CdO:2%In films

The optical bandgap values obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ to $\alpha=0$. These plots are given in Figure 5. Better linearity was observed in the former case and it was determined that all films have a direct band transition. The optical band gap of the films slightly increases with increasing In doping and molar concentration. For CdO film E_g equals to 2.28 (eV) and the E_g values of In (2%) doped CdO films with different molarities equal to 2.3 , 2.35 and 2.45 (eV), this slight shift of the band gap with increasing molarities is mainly related to the increasing of carrier density (Kose, S., F. Atay, V. Bilgin and I. Akyuz, 2009; Kumaravel, R., *et al.*, 2010).

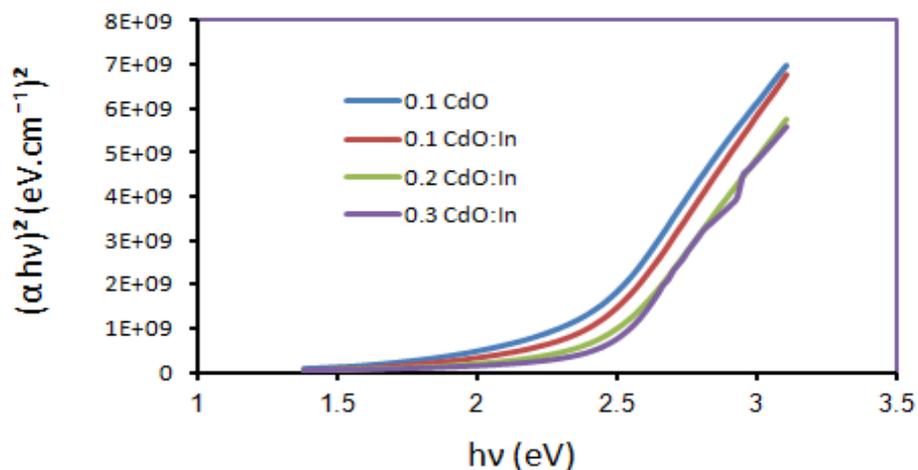


Fig. 5: The $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ of various molar concentration for CdO and CdO:2%In films

The optical reflectance spectra of the films whose values are roughly estimated from the below equation [29], are shown in Figure 6. As seen in the figure, the reflectance values of the films in the visible region change with molar concentrations.

$$T+A+R=1$$

(5)

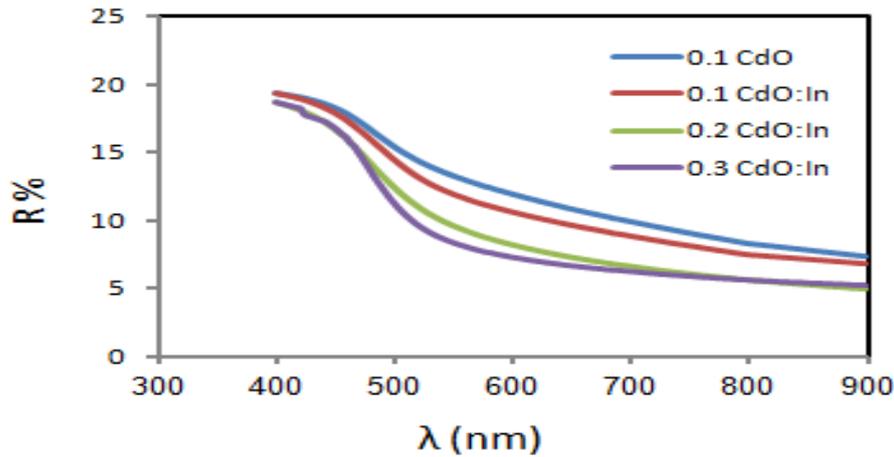


Fig. 6: Optical reflectance spectra of various molar concentration for CdO and CdO:2%In films The extinction coefficient of all films was calculated from equation (Benramdane, N., *et al.*, 1997; Ferro, R., *et al.*, 2000):

$$k = \alpha\lambda/4\pi \quad (6)$$

The variation of the extinction coefficient with wavelength of all films is shown in Figure 7. It was clearly seen that the extinction coefficient decreases with the increasing in wavelength and molar concentration.

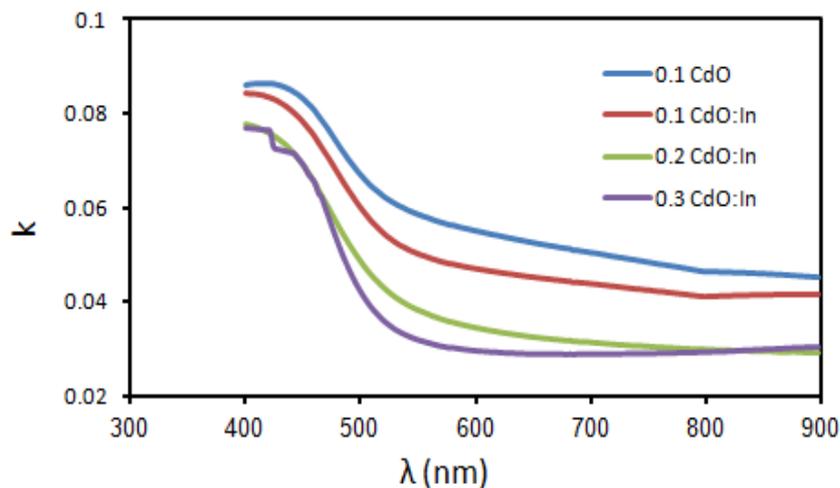


Fig. 7: Extinction coefficient variation with wavelength of various molar concentration for CdO and CdO:2%In films

Refractive index was calculated because it is very important as a significant factor in optical communication and in designing devices. A roughly measurements could be estimated form the below formula (Ferro, R., *et al.*, 2000), which depend only on transmission. The n values of all films were plotted versus the wavelength in Figure 8. It is clear that the n values for all films decrease with the increasing in wavelength and molar concentration.

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (7)$$

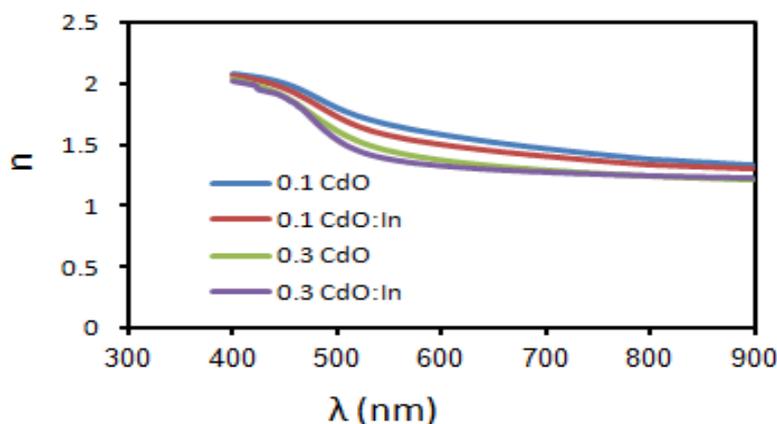


Fig. 8: Refractive index variation with wavelength of various molar concentration for CdO and CdO:2%In films

All the measured and calculated values of optical properties and constants of various molar concentration for CdO and CdO:2%In films at the fundamental edge were tabulated in Table 3.

Table 3: All the measured and calculated values of optical properties and constants of all films

Material	Molarities	T%	A%	R%	n	k	$\alpha \times 10^4 \text{ cm}^{-1}$	E_g
		$\lambda = 550 \text{ nm}$						
CdO	0.1M	73.07	13.6	13.3	1.65	0.058	1.3348	2.28
CdO:2%In	0.1M	76.3	11.7	11.9	1.57	0.050	1.1479	2.3
CdO:2%In	0.2 M	81.4	8.9	9.6	1.44	0.038	0.8727	2.35
CdO:2%In	0.3 M	84.1	7.4	8.3	1.37	0.032	0.7323	2.45

Conclusions:

Transparent and conducting In-doped cadmium oxide films were deposited on glass substrates at $350 \pm 10 \text{ }^\circ\text{C}$ by spray pyrolysis method. The effect of In doping and increasing molarities concentration on structural and optical properties were investigated. The polycrystalline In-doped CdO films were confirmed to be cubic crystal structure. All films exhibit good optical transmittance with increased bandgap values of all films when they were compared with the corresponding value of CdO film. For CdO film E_g equals to 2.28 (eV) and the E_g values of In (2%) doped CdO films with different molarities equal to 2.3, 2.35 and 2.45 (eV). The XRD measurements gives an indication that the crystallite size lie within the nano crystal range of (18.5-30.8nm). From the results it may be said that nano-crystalline CdO: In material can be grown by our locally developed spray pyrolysis method.

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