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Structural, optical and electrical properties of indium doped cadmium oxide thin films

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ABSTRACT

Conducting and transparent indium doped CdO thin films were prepared by spray pyrolysis on a glass substrate with various concentration of indium (2–8 wt%) in the spray solution. The optical and structural properties of indium doped and undoped CdO films were studied utilizing optical transmission, X-ray diffraction and atomic force microscope. X-ray analysis shows that the doped and undoped CdO films are preferentially orientated along (111) crystallographic directions. Increase of indium doping concentration increases the films packing density and reorient the crystallites along (1 1 1) plane. There is a decrease in the optical transmissions for all films with the decrease in wavelength. The light transmission of CdO films increases as In doping level increases. The optical band gap value of CdO was equal to 2.55 eV and it was increase with doping concentration and reaches a maximum value of 2.65 eV at 4 wt% indium doping. Low resistivity achieved in the present study was found to be 0.9×10^{-3}(Ω.cm) at 4wt% In doping.

KEYWORDS

Thin film;
Structural properties;
CdO;
CdO:In;
Optical properties;
Hall measurements.

INTRODUCTION

Transparent conducting oxides (TCOs) are materials that possess both high electrical conductivity, high optical transparency (> 80%) in the visible light region of the electromagnetic spectrum. These are remarkable materials in that the above properties are generally mutually exclusive and are hard to find in the same material. Cadmium oxide is a n-type semiconductor with non-stoichiometric composition due to the presence of either interstitial cadmium or oxygen vacancies, which act as doubly charged donors[1], with nearly metallic conductivity. One of the ways of tailoring the band gap is by synthesis a new semiconductor phases with large/small band gap semiconductors. The band gap of cadmium oxide can be thus tuned over a wide range from 1.1 eV to 3.3 eV by alloying with suitable materials. These alloyed semiconductors have a number of interesting applications in electrochemical or photoelectrochemical devices, phototransistors, photodiodes, gas sensors, etc.[2-4].

CdO thin films have been prepared by various physical and chemical deposition techniques such as pulsed laser deposition[5,6], spray pyrolysis[7-9], sol–gel[10,11], DC magnetron sputtering[12-14], RF sputtering[15], chemical bath deposition[16] and thermal evaporation[17-19].

In this work we have employed spray pyrolysis to prepare CdO:In films because of its simple and inexpensive experimental arrangement, ease of adding various doping material, reproducibility, high growth rate and mass production capability for uniform large area coatings, which are desirable for industrial and solar cell applications[20,21]. In the past years, CdO has received a considerable attention as the transparent electrode of CdTe-based thin film solar cells[22,23], because of its electrooptical properties compared with the traditional TCOs, such as SnO2:F and ZnO:Al[24]. In this paper, we are reporting the effect of In doping on structural, optical and electrical properties of In doped and undoped CdO thin films.

EXPERIMENTAL PROCEDURE

Spray pyrolysis deposition technique was used to prepare CdO and CdO:In thin films on glass substrates. An 0.1M solution of cadmium acetate Cd(CH3COO)2.2H2O diluted with methanol and water in the ratio of 1:1 was used to prepare CdO solution. CdO:In thin films were prepared by doping CdO solution in ratio (2-8%) of $InCl_3$ and water mixture with 0.1 M. The optimum deposition parameters were: The distance between the nozzle and the substrate was maintained at 31 cm, the substrate temperature was kept at 350°C and controlled within ±10°C by using an iron-constant thermocouple, nitrogen gas with a pressure of 4 bar, spray time (7 s) and the spray interval (70 s). The films thicknesses were measured by using Mlichlson Interferometer and found to be between (225-251)nm. The experimental details of mixed spraying solutions and the thicknesses of all films are listed in TABLE 1.

The crystalline structure of the films was confirmed by X-ray diffraction (XRD) with Cu Kα radiation (Rigaku Model, λ = 1.5406Å). The accelerating voltage 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, Cez200,7000Series, Metertec). The morphological properties of all films were investigated using (SPM model AA 3000 Angstrom Advanced Lns.,USA).

TABLE 1 : The mixed spraying solutions and the thicknesses of In doped & undoped CdO films.

Material	$Cd(CH_3COO)_2$. $2H_2O$(ml)	$InCl_3$ (ml)	Total (ml)	Thickness (nm)
CdO	100	0	100	225
CdO:In (2 wt.%)	98	2	100	251
CdO:In (4 wt.%)	96	4	100	220
CdO:In (6 wt.%)	94	6	100	238
CdO:In (8 wt.%)	92	8	100	234

RESULTS AND DISCUSSION

Structural properties

Figure 1 shows the X-ray diffraction (XRD) patterns of the prepared undoped CdO and CdO:In films. 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). XRD shows neither the formation of CdO_2 and In_2O_3 nor mixed phases even at higher In-doping level. It can be clearly seen that all films are preferentially orientated along (111) crystallographic directions and the preferential orientation peak for In doped films became sharper and more intense, especially for In doping level at 4%, compared to the pure CdO films. This may be attributed to the crystallinity of the CdO films being improved with In doping. Also, the structural parameters such as diffraction angle (2θ), lattice spacing (d), relative intensity of the peaks (I / I□), full width at half maximum (FWHM), intensity (I) and the phases identified along with (hkl) planes were evaluated from these spectra and presented in TABLE 2.

For all films, the grain size (D) was calculated from the full width at half maximum (FWHM) (β) of the preferential orientation diffraction peak by using the Scherrer equation[25,26]:

$$D=\frac{k.\lambda}{\beta.cos\theta} \qquad (1)$$

where *k* denotes the Scherrer constant (the shape factor of the average crystallite and can be considered *k* = 0.90, λ= 1.5418Å is the wavelength of the incident Cu *Kα* radiation. Larger D and smaller β values indicate better crystallization of the materials. According to TABLE 3, all CdO:In films have better crystallinity levels as increasing in the doping level. Moreover the texture coefficient TC (hkl) is introduced to characterize the preferential crystallite orientation along the (hkl) direction defined as[27]:

$$TC(hkl) = \frac{\frac{I(hkl)}{I}\square(hkl)}{N^{-1}\sum_N\left[\frac{I(hkl)}{I}\square(hkl)\right]} \quad (2)$$

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

Material	2θ(deg)	d(Å)	I / I□	FWHM (deg)	I(counts)	Identification with (hkl) values
	32.9696	2.71461	100	0.41410	114	(111) CdO
CdO	38.2771	2.34952	62	0.53410	71	(200) CdO
	55.2581	1.66104	17	0.33570	19	(220) CdO
	33.0703	2.70657	100	0.25930	210	(111) CdO
CdO:In (2 wt.%)	38.3662	2.34427	74	0.25580	156	(200) CdO
	55.3596	1.65824	20	0.22560	41	(220) CdO
	33.0981	2.70438	100	0.27180	442	(111) CdO
CdO:In (4 wt.%)	38.3912	2.34280	66	0.31820	293	(200) CdO
	55.3913	1.65736	17	0.25570	77	(220) CdO
	33.0820	2.70564	100	0.25900	288	(111) CdO
CdO:In (6 wt.%)	38.3752	2.34374	74	0.29370	214	(200) CdO
	55.3291	1.65908	24	0.38620	70	(220) CdO
	33.0917	2.70487	100	0.20170	416	(111) CdO
CdO:In (8 wt.%)	38.4063	2.34192	69	0.21950	287	(200) CdO
	55.3892	1.65742	20	0.28360	82	(220) CdO

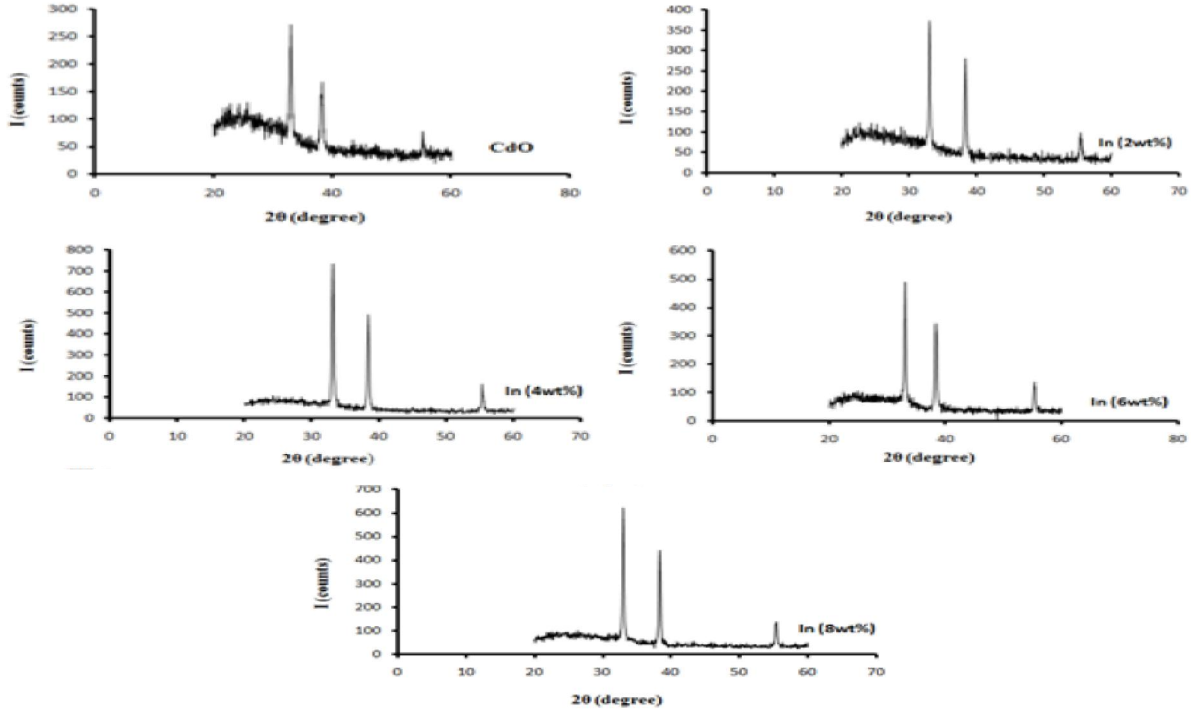

Figure 1 : The x-ray diffraction (XRD) patterns of the prepared undoped CdO and CdO:In films.

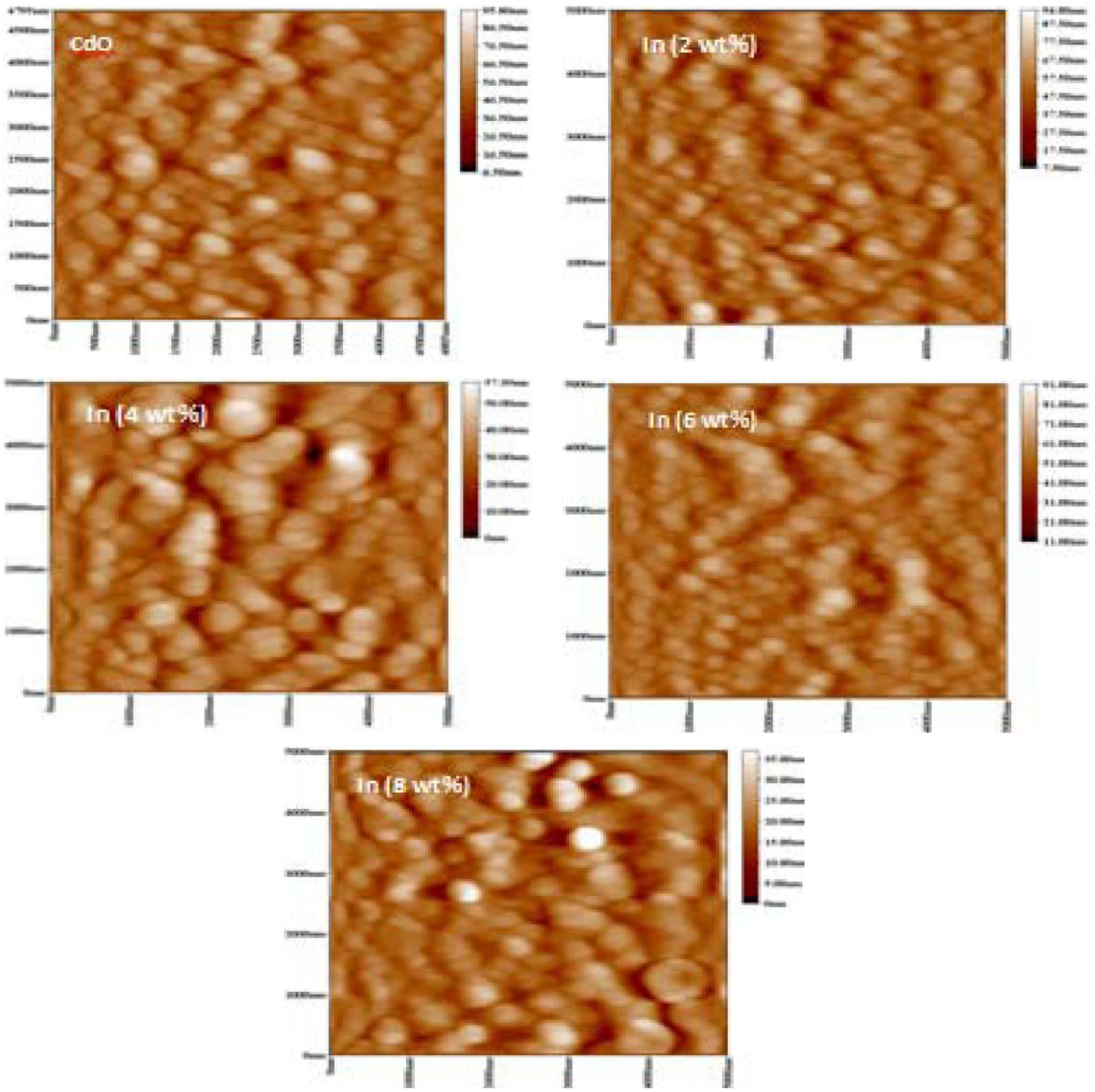

Figure 2 : AFM images of In doped and undoped CdO films.

TABLE 3. It can be observed that the highest TC (hkl) value is in (111) plane for In 4 wt% thin film.

The calculated lattice constant for the dominant peak of (1 1 1) of CdO is averaged to a = 4.6888 Å which is close to the reported value a□= 4.695Å[28]. Additionally, to have more information on the amount of defects in the films, the dislocation density (δ) was evaluated from the formula[29]:

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

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 3 that the δ value of CdO films is decreased with In doping. This means In doping decreases the defects in the CdO films and improves crystallite quality. Similar results have been reported by Kose *et al*.[30].

AFM images of pure and In doped cadmium oxide films are shown in Figure 2. The white regions in this figure represent the formation of agglomerated grains one on the top of the other. For these regions, we think that neighboring grains come together forming large clusters. So grains in the white regions are larger in size as compared to others. From all of these interpretations, film growth mechanism is thought to be formed firstly layer by layer and then island growth type. The In doped films show smooth surface compared to the cadmium oxide films. The 500 nm× 500 nm images are utilized for measuring the average roughness (Ra) and root mean square roughness surface (Rq) of the films. The (Ra) and (Rq) of the pure CdO film are measured to be 7.05 nm and 9.04 nm respectively. Further, the (Ra) and (Rq) of the samples decreases with increase in doping concentration. These results represented in TABLE 4, are closely similar to the results which had been reported by Kumaravel *et al.*[31].

TABLE 3 : FWHM (β), texture coefficient (TC), the grain size (D) and the dislocation density (δ) and lattice constant(a) of the CdO & CdO:In films.

Material	Preferential Orientation	$\beta\times10^{-3}$ (rad)	TC	D (nm)	$\times\delta\ 10^{-6}$ ($Å^{-2}$)	a(Å)
CdO	(111)	7.2237	1.43	20	24.94	4.7071
CdO:In (2 wt.%)	(111)	4.5233	1.31	31.9	9.77	4.6877
CdO:In (4 wt.%)	(111)	4.7414	1.49	30.5	10.74	4.6839
CdO:In (6 wt.%)	(111)	4.5181	1.24	32.0	9.75	4.6861
CdO:In (8 wt.%)	(111)	3.5185	1.34	41.1	5.91	4.6848

TABLE 4 : The roughness(Ra) and root mean square roughness surface (Rq) of the doped & undoped films.

Material	Ra(nm)	Rq(nm)
CdO	7.05	9.04
CdO:In(2 wt.%)	6.86	9.04
CdO:In(4 wt.%)	5.61	7.3
CdO:In(6 wt.%)	5.42	6.99
CdO:In(8 wt.%)	3.63	4.85

Optical properties

Optical transmittance spectra of the undoped and In doped CdO films in the range of 300–900 nm are presented in Figure 3, measured at room temperature in air. As seen in this figure, the optical transmissions of all films decreased with decrease in wavelength and the light transmission of CdO films increases as In doping level increases. These spectra show that adding In to CdO improves the transmittance for all the deposited samples. The undoped films show a transmittance of 62.8% (800 nm) and the doping increases the transmittance value up to 81.3% (800 nm) for the 8 wt.% In doping. This effect of In 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.

The ability of a material to absorb light is measured by its absorption coefficient. The absorption coefficient (α) is calculated using the equation[32]:

$$\alpha = \ln(1/T)/d \tag{4}$$

Where T is transmittance and d is film thickness. The variation of the optical absorbance coefficient with wavelength is shown in Figure 4, It was clearly seen that the absorbance increases with the decrease in wavelength and decreases with the increasing In doping concentration. The sharp increase in absorbance at the wavelength $\lambda < 550$ nm is due to the onset of interband transitions at the fundamental edge. the optical band gap 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 the increasing In doping. For CdO film Eg = 2.55(eV) and the Eg values of In (2-8%) doped CdO films equal to 2.6,2.65,2.62 and 2.58(eV),this slight shift of the band gap with the increase in In doping is mainly

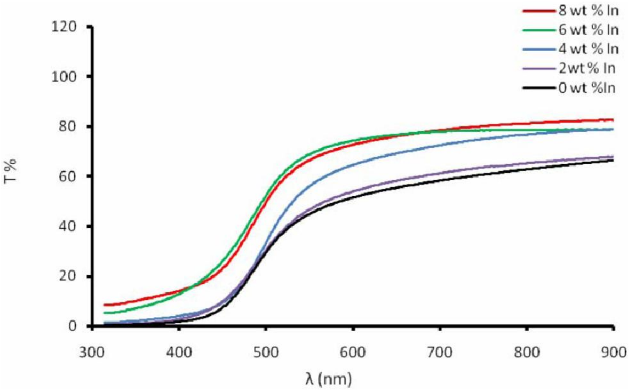

Figure 3 : Optical transmittance spectra of In doped and undoped CdO films.

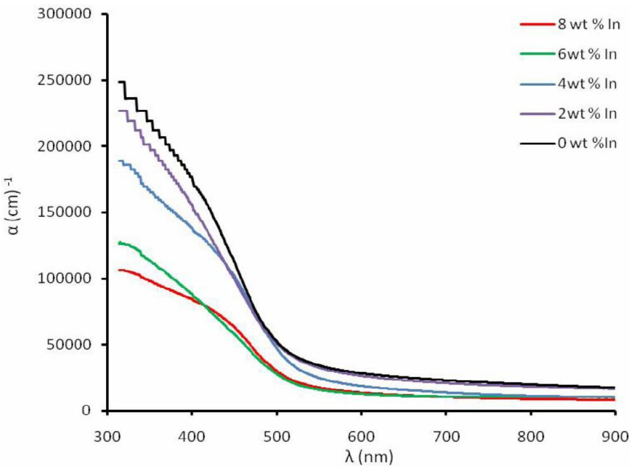

Figure 4 : The variation of the absorption coefficient with wavelength.

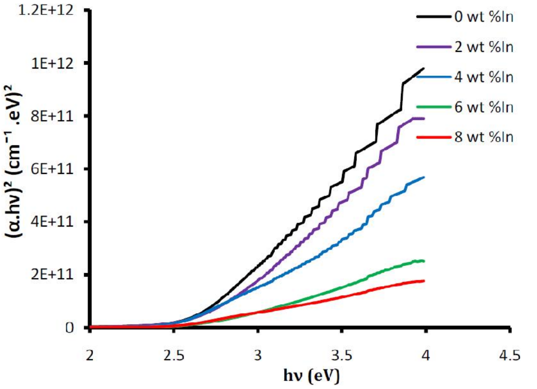

Figure 5 : The (αhν)2 versus photon energy (hν) for In doped and undoped CdO films.

related to the increase of carrier density[30,31].

Electrical properties

Hall voltage measurement was made to determine some electrical properties for un-doped and In doped samples at room temperature in a constant magnetic field of 0.55T. Hall constant (R_H), the conductivity (σ), electrical resistivity (ρ), carrier Concentration (Ne) and mobility (μ) have been calculated from Hall voltage and the obtained values are listed in TABLE 5. Hall measurement indicates that CdO and In-doped CdO are n-type material and electrons are the majority carrier of current. From Table, it is clear, that conductivity and carrier concentrations increased with the increasing of doping levels for all the films. This indicates that the dopant In ions in CdO film can either enter into the crystalline structure of CdO existing mainly in substitutional state or adsorbed in grain boundary regions. Since In ions substituting Cd ions in Cd lattice can liberate more conducting electrons in the conduction band,the increase of In concentration to certain level can significantly enhance the concentration of electrons and hence the carrier concentration[33]. The variation of electrical resistivity (ρ) as a function of In-dopoing level is shown in Figure 6. From the figure one can observe that the resistivity of the films was found to decrease with increasing In-doping. These changes are resulted from the variation in Ne and carrier scattering by different microstructural defects, grain boundaries, and ionised impurities. The CdO film possesses a resistivity of $3.925\times10^{-3}\Omega$.cm which decreases with increase in In doping concentration up to 4 wt%. Thus the doping substantially reduces the resistivity to $0.925\times10^{-3}\Omega$.cm for 4 wt% of In. On doping, cadmium might be progressively replaced by the indium and since In belongs to the group III, it contributes an additional electron to the conductivity. When In concentration is increased beyond 4 wt%, In moves toward the grain boundaries causing a high dispersion of free carriers through grain boundaries, thus contributing to an increase in resistivity. However, the resistivity of doped and undoped CdO, in the present work, is larger than those values mentioned in some other references due to different method and procedure of preparation[31]. From TABLE 5, the mobility value increases with increasing doping at first until 4 wt%. Then at higher doping levels, the mobility values were decreased. The decrease in mobility at higher doping concentration is due to the loss of crystallinity and the presence of neutral impurity centers.

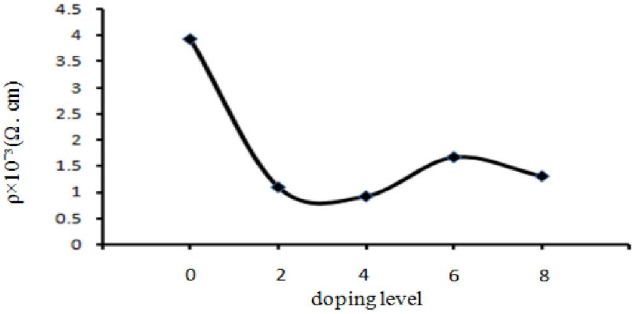

Figure 6 : The variation of electrical resistivity (ρ) as a function of In-doping level.

TABLE 5 : The hall constant(R_H), the conductivity (σ), electrical resistivity(ρ), carriers concentration(Ne) and mobility(μ) of In doped & undoped CdO thin films.

Material	$R_H\times10^{-2}$ (cm^3/C)	$\sigma\times10^{2}$ $(\Omega.cm)^{-1}$	$\rho\times10^{-3}$ (Ω.cm)	$Ne\times10^{19}$ (cm^{-3})	μ($cm^2/V.s$)
CdO	10.18	2.54	3.92	6.14	25.9
CdO (2 wt%)	8.05	9.09	1.1	7.76	73.2
CdO (4 wt%)	7.74	10.81	0.9	8.07	83.6
CdO (6 wt%)	6.46	5.97	1.67	9.67	38.6
CdO (8 wt%)	5.57	7.63	1.31	11.22	42.5

The present work proves that light doping with In improves the dc-conduction parameters of CdO. These results were in good agreement with Dakhel[34,35].

CONCLUSIONS

Transparent and conducting In-doped cadmium oxide films were deposited on glass substrates at 350±10 C° by spray pyrolysis method. The effect of In doping concentration on structural,optical and electrical properties were investigated. The polycrystalline In- doped CdO films were confirmed to be cubic crystal structure with no evidence of $In_2O_3$and CdO_2 or mixed phases. In-doped CdO films exhibit good optical transmittance with increased bandgap value was compared with the corresponding values of CdO film. The band gap value of 2.55eVfor CdO increases and reaches a maximum value of 2.65 eV at 4 wt% In-doping. A minimum resistivity of 0.9×10^{-3} (Ω.cm) with maximum carrier mobility of 83.6(cm^2/V.s) is achieved at the optimum In-doping level of 4 wt%. The minimum resistivity with high transmittance in visible range for In-doped CdO films make them extensively used in optoelectronic devices. The XRD and AFM measurements gives an indication that the crystallite size lie within the nanocrystal range

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