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ENHANCED OPTICAL TRANSMITTANCE OF SPRAY DEPOSITED ZINC OXIDE THIN FILMS FOR OPTOELECTRONIC APPLICATIONS

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ABSTRACT
Transparent zinc oxide thin films (undoped and Mo doped) were coated on glass substrates at the substrate temperature of 400°C using spray pyrolysis set up. The various Mo doping concentrations for the Mo doped thin films are 0.25wt.%, 0.5wt.%, 0.75wt.% and 1wt.%. Prepared thin films were characterized by X-ray Diffraction (XRD) and UV-Vis Spectroscopy techniques. Thicknesses of the prepared films were determined using gravimetric method. XRD of the films shows that ZnO belongs to the hexagonal wurtzite structure. Preferred growth orientation for undoped and Mo doped ZnO thin films is along (002) direction, except for the 0.5wt.%Mo:ZnO thin film where the (101) peak becomes prominent. The XRD intensity of the (002) peak decreases with increasing Mo doping concentration for 0.25wt.% and 0.5wt.%, after which it increases for 0.75wt.% and 1wt.%. Crystallite sizes and lattice parameters for the ZnO and Mo:ZnO thin films were also evaluated. Optical studies of the prepared films show an average visible transmittance (AVT) of about 88% recorded in the 380nm to 800nm wavelength region. Optical bandgap for all the films were also reported. Slight increase in the bandgap of ZnO is observed with increasing Mo doping concentration.
Keywords: average visible transmittance, spray pyrolysis, thin films, lattice parameters, optical bandgap.

INTRODUCTION

Over the years, there has been increasing demand in low cost transparent conductive oxides (TCO) films, due to their optoelectronic properties in such devices as light emitting diodes, flat panel displays, window layers in heterojunction solar cells, heat mirrors e.t.c. (Mohammad et al, 2006; Swapna and Kumar, 2013). ZnO is one of the promising TCO due to its direct and wide bandgap (about 3.37eV) and large exciton binding energy (about 60meV at 300K), low cost, good optical and piezoelectric behavior compared to other TCO like ITO, SnO_3, Cd_2SnO_4 (Souissi et al, 2014; Bougarine *et al,* 2003). ZnO thin films can be prepared by various techniques, some of which include pulsed laser deposition (Cao et al, 2011), magnetron sputtering(Yoon et al, 2008), sol gel dip coating (Ramesh et al, 2013), reactive electron beam evaporation (Iqbal *et al,* 2013), sol gel spin coating (Thambidurai, 2014) and spray pyrolysis (Gokulakrishnan *et al,* 2011; Jagadesh and Pearton, 2006; Benramache *et al*, A very small amount of Mo doping can possibly give enough free carriers in the ZnO film because of the high valence difference between 2014; Swapna and Kumar, 2012; Gokulakrishnan *et al.,* 2011).

Although ZnO has a high transparency, it equally has a low conductivity. Reports have shown that doping ZnO with various impurity materials at different doping levels in the film can lead to improved electrical conductivity without compromising optical transmittance. For instance zirconium doping showed a lowest resistivity of $2\times10^{-3}\Omega$cm at 3wt% (Gokulakrishnan *et al.,* 2011), doping of cobalt showed a conductivity of $9.27(\Omega cm)^{-1}$ at 2wt% (Swapna and Kumar, 2012) and doping of molybdenum showed a resistivity of $6.22\times10^{-2}\Omega$cm (Benramache *et al.,* 2014). In Mo doped ZnO, Mo either substitutes Zn in the host matrix or it acts as an interstitial atom. The substitution of Zn with Mo is possible due to smaller radius of Mo (0.062nm) compared to Zn (0.083nm) (Swapna and Kumar, 2012).

In the present work we investigated the effect of very low Mo doping concentrations in ZnO film deposited using spray pyrolysis set up. Mo^{6+} and Zn^{2+}.Therefore Mo([Kr]: $4d^5 5s^1$) can donate four electrons to the free carriers in the ZnO matrix. The spray pyrolysis technique in

comparison to other chemical deposition techniques has several advantages such as high purity and excellent control of chemical uniformity in multi-component system. Deposited films were subjected to various characterization studies in order to investigate the doping effects on the structural and optical properties of the films.

Experimental detail

Pure ZnO and Mo doped ZnO thin films were coated on glass substrates at 400°C by spray pyrolysis method. A homogenous solution was obtaind by dissolving 0.1M zinc acetate dihydrate ($Zn(CH_3COOH)_2.2H_2O$) and ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) in double distilled water and methanol (in the ratio 3:1) using compressed air as carrier gas. As explained in our previous work, the following optimization set up was maintained throughout the experiments; the spray nozzle-substrate distance (25cm), spray angle (45°), carrier gas pressure (40Kgcm^{-2}), spray time (1sec) and spray interval (20sec) (Abdullahi et al, 2015; Abdullahi and Ramamurthi, 2015).

Structural properties of the prepared films were studied PANalytical X`Pert PRO X-ray diffractometer (CuKα radiation, λ=1.5405Å), 2Θ range of 0° - 90°. Optical properties of the deposited films were investigated using double beam spectrophotometer (Ocean Optics) in the wavelength range of 300-1000 nm.

RESULTS AND DISCUSSION

Structural studies

Fig. 1 shows the X-ray diffraction patterns for ZnO and Mo:ZnO thin films. The JCPDS card no. 89-1397 confirms that the films belong to the hexagonal wurtzite structure with (002) preferential orientation. The undopedZnO film has (002) peak corresponding to 2Θ =34.30° as the highest peak intensity followed by the (101) peak corresponding to 2Θ=36.08°. Other peaks include the (102), (110), (103) and (113) diffraction. The (002) peak intensity decreases with increase in the Mo doping concentration from 0.25 wt.% to 0.5 wt.%. It then increases progressively for 0.75wt.% and 1wt.%. The intensity of the (002) is maximum for 1wt.% compared to other doping concentrations. All peaks seen in the XRD pattern belong to ZnO as confirmed from the JCPDS card number stated above.

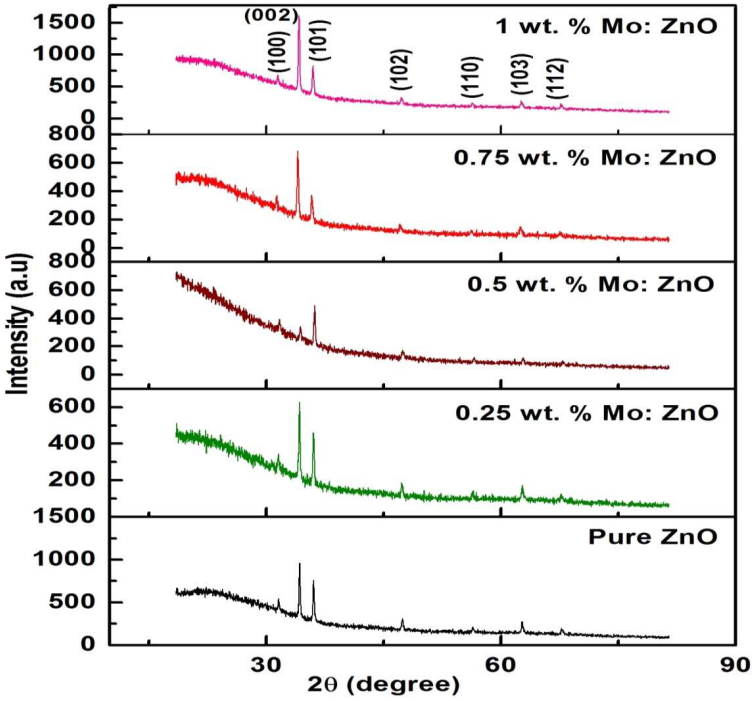

Fig.1. XRD patterns of undoped and Mo doped ZnO thin films.

The lattice parameters '*a*' and '*c*' of the deposited ZnO and Mo:ZnO thin films were estimated from (002) and (001) XRD peaks respectively and are presented in Table 1. A slight change in the '*a*' and '*c*' values is due to the change in the 2Θ values of the peaks. Thus molybdenum incorporation into the ZnO matrix leads to a slight change in the lattice parameters. Crystallite size of the deposited thin films were obtained from Scherrer's formula (Cullity, 1967).

$$D = \frac{C\lambda}{\beta \cos\Theta} \quad (1)$$

Where C is correction factor (0.9), λ is the wavelength of X-rays (λ=1.5405Å) and β is the full width half maximum (in radian). The crystallite size calculated from the (002) peak of the deposited Mo:ZnO thin films varies with doping concentration from ~32.6nm to 45.1nm.The lattice parameters for the hexagonal structure are obtain from the formula(Abdullahi et al, 2015).

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \quad (2)$$

where d is the interplaner distance and (hkl) refers to the Miller indices.

The interplanaer distance is calculated using the Bragg's relation for first order reflection (Gokulakrishnan *et al,* 2011).

$$d = \frac{\lambda}{2\sin\theta} \quad (3)$$

where Θ is the glancing angle.

Table 1: Structural parameters for ZnO and Mo:ZnO thin films for (002) peak

Mo:ZnO (wt.%)	2Θ (°)	FWHM (°)	d - spacing (Å)	D (nm)	Lattice Parameter (Å)	
					a	***c***
0	34.30	0.18	2.61	45.08	3.27	5.22
0.25	34.28	0.19	2.61	44.57	3.27	5.23
0.50	34.42	0.26	2.60	32.58	3.25	5.21
0.75	34.16	0.22	2.62	38.12	3.29	5.24
1.00	34.23	0.20	2.62	42.50	3.27	5.23

Optical studies

Figure 2 shows the optical transmittance of ZnO and Mo:ZnO thin films in the range 200-1200nm of wavelength. An average visible transmittance (AVT) of about 88% is recorded in the 380nm - 800nm wavelength region. Increase in the transmittance is observed with an increase in Mo doping concentration (Table 2). Absorption coefficient for the deposited films is calculated using the relation (Gokulakrishnan et al, 2011).

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \quad (4)$$

where t is the film thickness and T is the transmittance of the film.

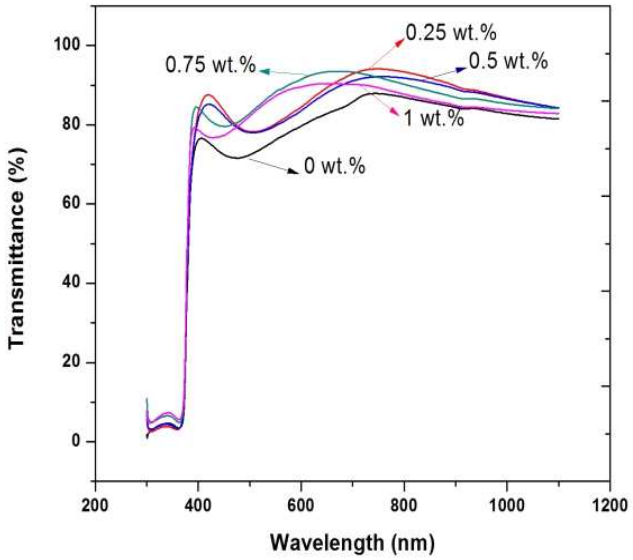

Figure 2: Optical transmittance of ZnO and Mo:ZnO thin films

Table 2: Average and maximum transmittance of ZnO and Mo:ZnO thin films.

Mo doping Co concentration (wt.%)	Average Visible transmittance (%) 380nm-800nm	Maximum Optical transmittance (%)
0	79.90	88 (700nm)
0.25	86.66	95 (750nm)
0.50	85.42	90 (750nm)
0.75	88.46	94 (650nm)
1.00	86.15	89 (650nm)

The direct bandgap of the films is obtained using the formula (Gokulakrishnan et al, 2011).

$$\alpha h\nu = B\left(h\nu - E_g\right)^{1/2} \quad (5)$$

where$h\nu$ is the photon energy, E_g is the optical bandgap and B is a constant.

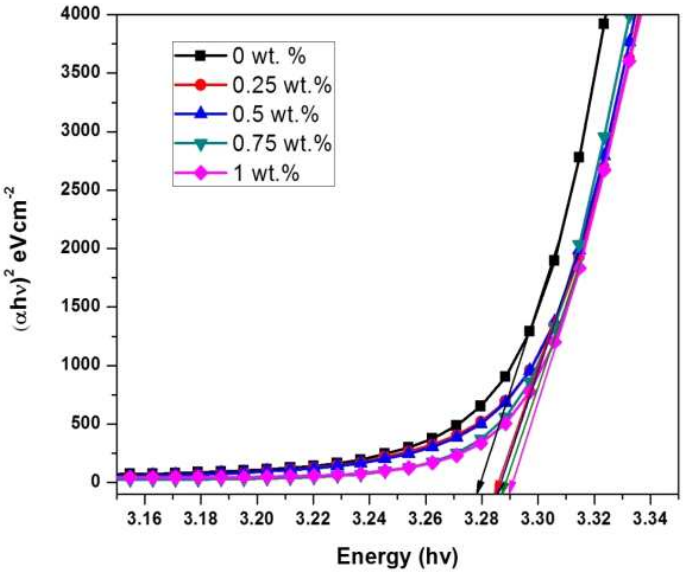

Figure 3: Optical bandgap values for ZnO and Mo:ZnO thin films

Table 3 Optical bandgap values for ZnO and Mo:ZnO thin films.

Mo doping Concentration (wt.%)	0	0.25	0.50	0.75	1.00
Optical Bandgap (eV)	3.278	3.285	3.286	3.288	3.290

Though Mo doping does not appreciably change the optical bandgap of the ZnO film, a slight increase is observed with increasing Mo doping level.

CONCLUSION

Pure ZnO and molybdenum doped zinc oxide thin films were coated on glass slide at 400°C using spray pyrolysis method. XRD pattern for the deposited films show a (002) preferred growth orientation. The intensity of the (002) peak initially decreases with Mo doping level up to 0.5 wt.%, after which it increases for 0.75 and 1 wt.% Mo doping concentration. All peaks are due to ZnO. The films belong to the hexagonal wurtzite structure of ZnO. UV-Vis spectra show an average visible transmittance (AVT) of about 88% recorded in the 380nm - 800nm wavelength region. Also a slight increase in the bandgap of ZnO is observed with increasing Mo concentration.

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