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A Study on Low Cost-Highly Transparent and Conductive Molybdenum Doped Zinc Oxide Thin Films Deposited by Spray Pyrolysis Technique

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Abstract: Pure zinc oxide (ZnO) and Molybdenum doped zinc oxide (Mo:ZnO) thin films were deposited at 673K on micro slide glass substrates using spray pyrolysis technique. Deposited thin films are characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and UV-Visible Spectroscopy techniques. X-ray diffraction analysis of the ZnO films confirm the formation of hexagonal wurtzite crystal system and the preferred growth orientation is along (002) plane for pure and Mo doped (0.25 wt.%, 0.75 wt.% and 1 wt.%) ZnO films. For the 0.5 wt.% Mo:ZnO thin film, the (101) peak becomes prominent. The XRD intensity of the (002) peak decreases with increasing Mo doping concentration for 0.25 wt.% and 0.5wt.% then the intensity of (002) plane increases for 0.75 wt.% and 1 wt.% of Mo doping. Lattice parameter, dislocation density and strain were evaluated for the pure and Mo:ZnO thin films. Scanning Electron microscope images show nearly uniform distribution of grains on the surface of the pure and molybdenum doped zinc oxide films (Figure 1). Atomic force microscopy results show that the root mean square roughness decreases with increasing Mo concentration for the film. An average visible transmittance (AVT) of about 88% is recorded in the visible range of 400-800 nm wavelengths. Slight increase in the bandgap of ZnO is observed with increasing Mo.

Keywords: Optical Transmittance, Spray Pyrolysis, Hexagonal Wurtzite, Lattice Parameters, Optical Bandgap

1. Introduction

Due to the numerous applications of Zinc Oxide (ZnO) in many areas, it has drawn the attention of many researchers over the years [1, 3-10]. ZnO thin film is a transparent conductive oxide (TCO) with direct optical bandgap of 3.37 eV and a large exciton binding energy of 60 meV at 300K [1]. ZnO is transparent in the visible range of sunlight and also operating in the UV to blue wavelengths [2]. This makes ZnO a promising material for applications in transparent electronics, optoelectronics and spintronic devices [2]. ZnO thin films can be deposited using variety of techniques which include pulsed laser deposition [3], magnetron sputtering [4], sol gel dip coating [5], reactive electron beam evaporation [6], sol gel spin coating [7], and spray pyrolysis [8-12].

Despite its high transparency, ZnO has low conductivity [9-11]. The conductivity of ZnO can be improved by doping proper dopants of various levels in the film. For instance; zirconium doping showed a lowest resistivity of 2×10^{-3} Ωcm at 3 at% [9], doping of molybdenum showed a resistivity of 6.22×10^{-2} Ωcm [10] and doping of cobalt showed a conductivity of 9.27 $(\Omega cm)^{-1}$ at 2 wt% [11]. In Mo doped ZnO, Mo^{6+} replaces Zn^{2+} in the ZnO crystal structure thus donating a maximum of four more free electrons. These additional electrons increase the electrical conductivity of Mo incorporated ZnO films. Also, the ionic radius of Mo^{6+} (0.041 nm) is close to that of Zn^{2+} (0.060 nm) and hence Mo^{6+} may easily replace Zn^{2+} in the host matrix and occupy less interstitial positions [12].

In this work we investigated th effect of Mo doping at

various concentrations in ZnO thin film deposited using a homemade spray pyrolysis setup. This technique has an advantage of large area coating and does not require a high vacuum environment. Deposited films were subjected to various characterization studies in order to investigate the Mo doping effects on the structural, optical and electrical properties of the ZnO films.

2. Experimental

ZnO and Mo doped ZnO thin films were deposited on the preheated glass substrates using spray pyrolysis technique. The precursor solution was prepared from 0.1 M zinc acetate dehydrate ($Zn(CH_3COOH)_2.2H_2O$) using double distilled water and methanol (in the ratio 3:1) as solvent. Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) was used as source for molybdenum. The Mo:ZnO films with four different doping concentrations (0.25, 0.5, 0.75 and 1 wt.%) were prepared. All films were deposited at 673K using compressed air as carrier gas. Throughout the experiments, the spray nozzle-substrate distance was maintained at 25 cm. Other parameters such as spray angle (45°), carrier gas pressure (4 $Kgcm^{-2}$), spray time (1 sec) and spray interval (20 sec) were kept constant.

Structural properties of the prepared films were studied using PANalytical X`Pert PRO X-ray diffractometer (Cu Kα radiation, λ = 1.5405 Å) in the 2Θ range of 0°-90°. The surface morphological studies of the films were carried out using scanning electron microscope (FEI quanta 200). Atomic force microscopy (Agilent Technologies SPM 5100 Pico LE) was used for surface roughness analysis of the films. Optical properties of the deposited films were investigated using double beam spectrophotometer (Ocean Optics) in the wavelength range of 300-1000 nm. Thicknesses of the films were determined using gravimetric method.

3. Results and Discussion

3.1. Structural Studies

X-ray diffraction patterns of ZnO and Mo:ZnO thin films presented in figure 1and comparison with JCPDS card no. 89-1397 confirms that the films belong to the hexagonal wurtzite structure with (002) preferential orientation. XRD peaks of the pure ZnO film show intense (002) peak at 2Θ = 34.30° and the (101) peak at 2Θ = 36.08°. Weak XRD peaks from the (102), (110), (103) and (113) planes are observed. The (002) peak intensity of pure ZnO decreases with increase in the Mo doping concentration 0.25 wt.% to 0.5 wt.%. Then the XRD intensity increases progressively for 0.75 wt.% and 1 wt.% Mo doping. The intensity of the (002) is maximum in the 1 wt.% Mo doped ZnO when compared to that of the other doped ZnO films. The Mo doping at various concentrations results in a shift in the 2Θ value of XRD peaks. Neither metallic zinc nor molybdenum oxide peaks are seen in the XRD pattern.

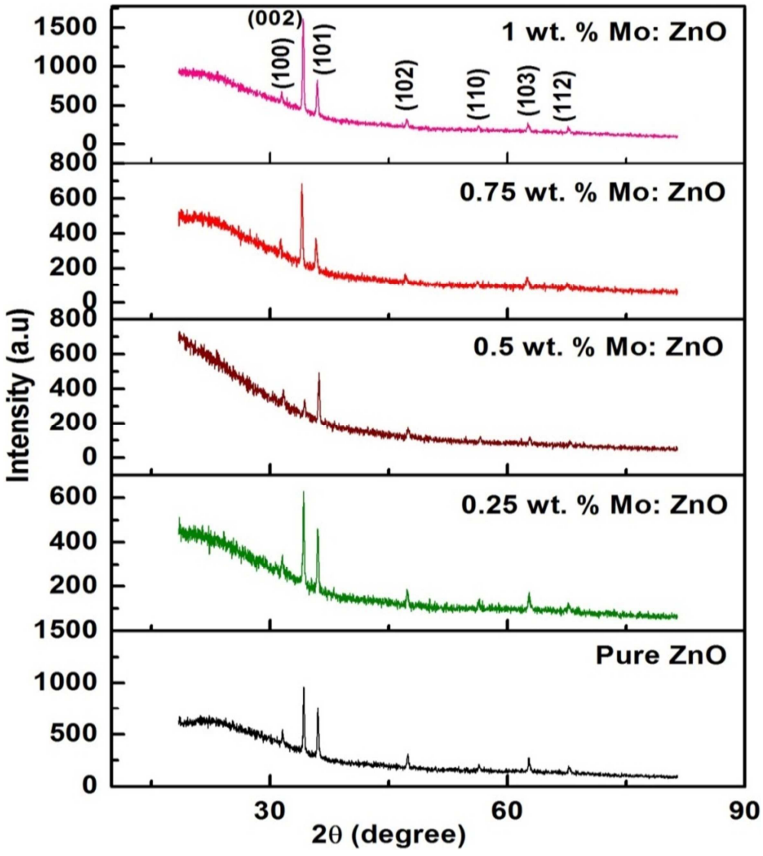

Figure 1. *XRD patterns of pure and Mo doped ZnO thin films.*

The lattice parameters '*a*' and '*c*' of the deposited ZnO and Mo:ZnO thin films were estimated from (001) and (002) XRD peaks respectively using the formula [13]

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

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

No appreciable change in the '*a*' and '*c*' values is observed (Table 1). Thus molybdenum incorporation into the ZnO matrix leads to only a slight change in the lattice parameters. Crystallite sizes of the deposited thin films were obtained from Scherrer's formula [13].

$$D = \frac{C\lambda}{\beta\cos\Theta} \quad (2)$$

where C is shape factor (0.9), λ is the wavelength of X-rays (λ = 1.5405 Å) 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 ~32.6 nm to 45.1 nm.

The strain (ε_z) in lattice along c-axis and the stress (σ_{film}) along the x-y plane for the hexagonal films are estimated using the formulae [1, 14-15]

$$\varepsilon_{z=}\frac{C_{film}-C_{bulk}}{C_{bulk}} \times 100\% \quad (3)$$

$$\sigma_{film=}-233 \times 10^9 \left(\frac{C_{film}-C_{bulk}}{C_{bulk}}\right) \text{Pa} \quad (4)$$

where C_{bulk} is the unstrained lattice parameter of ZnO and C_{film} is the lattice parameter of strained films calculated from XRD data. The negative values for the stress indicate that C_{film} is greater than C_{bulk} for all the films, hence the biaxial stress of the films is compressive [10].

Table 1. *Structural parameters of ZnO and Mo:ZnO thin films.*

Mo: ZnO (wt.%)	2Θ (°)	Dspacing (Å)	D (nm)	ε_z (%)	σ_{film} (GPa)	Lattice Parameters(Å)	
						a	*c*
0	34.30	2.61	45.08	0.34	-0.79	3.27	5.22
0.25	34.28	2.61	44.57	0.42	-0.98	3.27	5.23
0.5	34.42	2.60	32.58	0.04	-0.09	3.25	5.21
0.75	34.16	2.62	38.12	0.40	-0.93	3.29	5.24
1	34.23	2.62	42.50	0.56	-1.30	3.27	5.23

3.2. Morphological Studies

The scanning electron microscope images of the deposited ZnO and Mo:ZnO films are shown in Figure 2. All the films show nearly uniform grain distribution and elongated hexagonal structures. Thus the SEM images confirm the hexagonal wurtzite structure of ZnO. An average grain size of ~ 81.4 nm is obtained for the pure zinc oxide film. Various doping concentration of Mo changes the grain size of the film. The maximum value of the grain size is obtained for the 0.25 wt.% Modoping. The surface morphology and the grain size of the 1 wt.% Mo:ZnO thin film and the pure ZnO films seem to be nearly similar to each other.

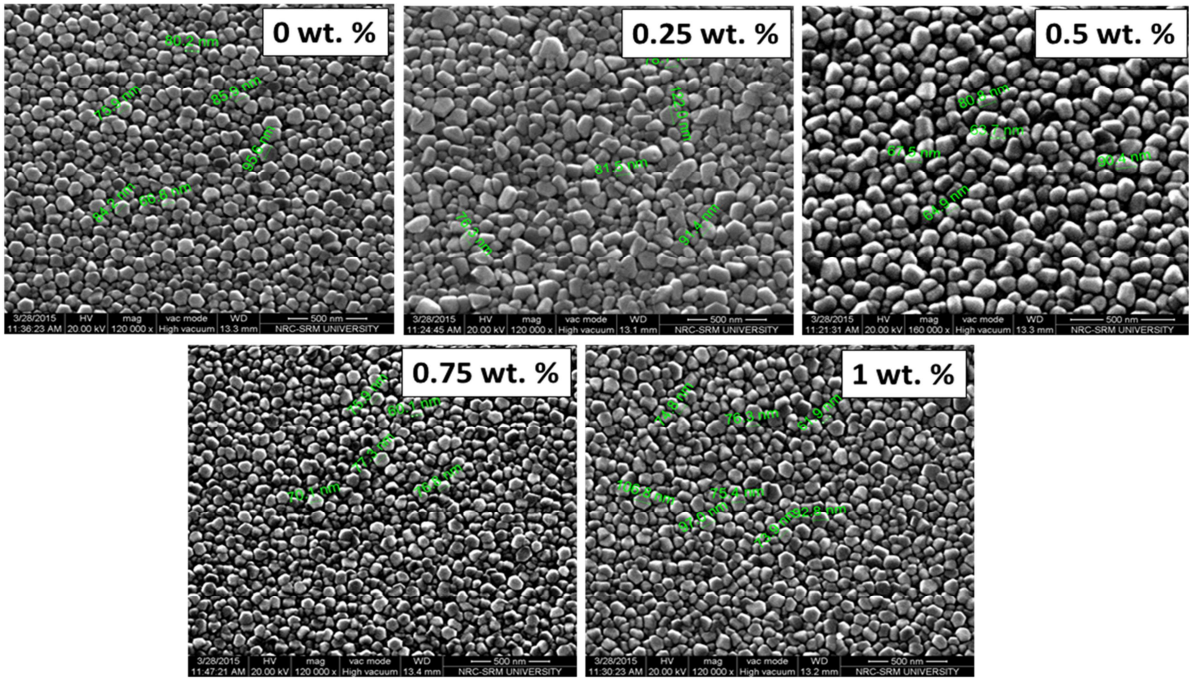

Figure 2. *SEM images of ZnO and Mo:ZnO at various doping concentrations.*

Figure 3 show 3D (1 µm × 1 µm) Atomic force microscope images of the pure and Mo doped ZnO thin films deposited at 673K (a = 0 wt.%, b = 0.25 wt.%, c = 0.5 wt.%, d = 0.75 wt.% and e = 1 wt.%). The root mean square (RMS) roughness obtained for each film is presented in Table 2. The pure ZnO film is having an average height of ~ 39.8 nm and an average roughness of about 7.6 nm. Mo doping reduces the average roughness of the film. Thus the RMS roughness decreases progressively with increasing Mo doping concentration. Relatively less RMS roughness of about 5.9 nm is observed for Mo:ZnO film doped for 1 wt.%.

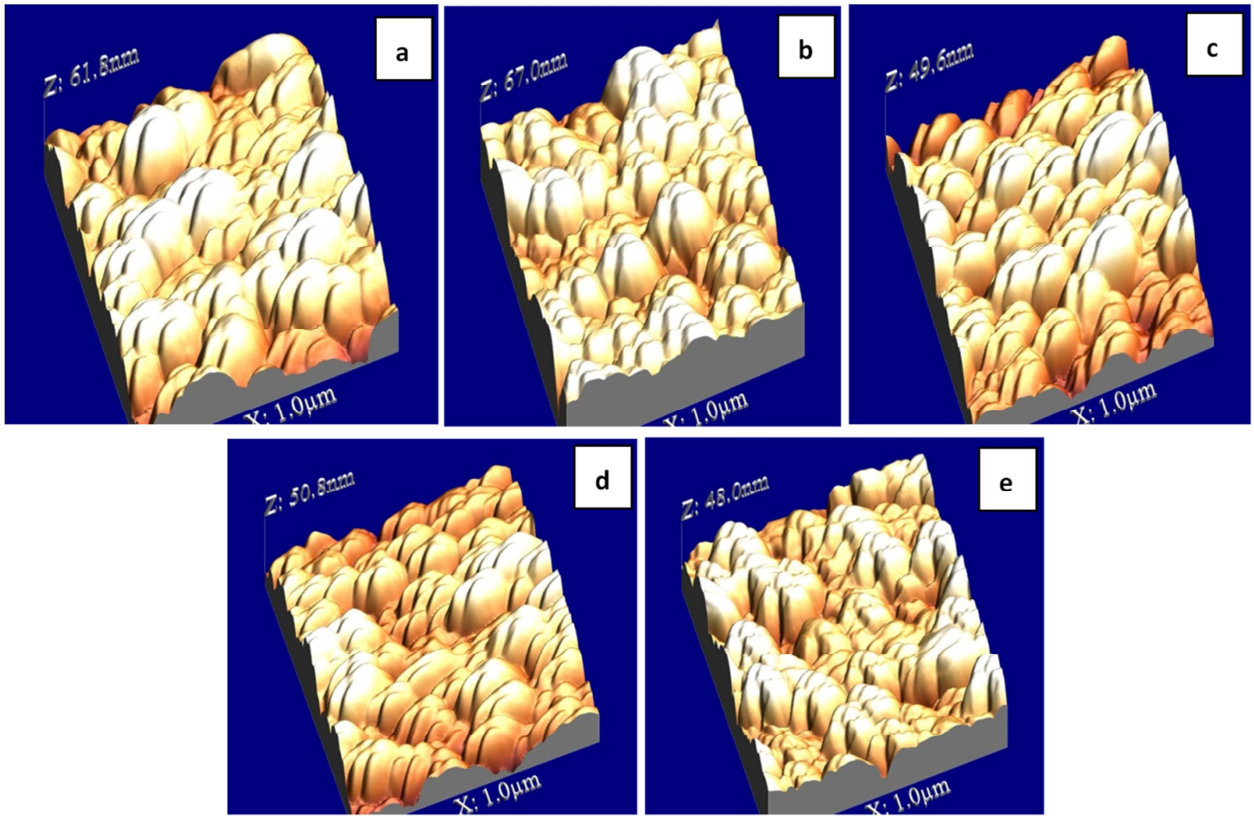

Figure 3. *3 D AFM images showing sample roughness for ZnO and Mo:ZnO thin films.*

Table 2. *RMS roughness of ZnO and Mo:ZnO thin films.*

Sample	RMS roughness(nm)
Pure ZnO(a)	9.67
0.25 wt.% Mo:ZnO(b)	9.02
0.5 wt.% Mo:ZnO(c)	8.76
0.75 wt.% Mo:ZnO(d)	7.78
1 wt.% Mo:ZnO(e)	7.16

3.3. Optical Studies

Figure 4 shows the optical transmittance of ZnO and Mo: ZnO thin films in the range 200-1200 nm of wavelength. An average visible transmittance (AVT) of about88% is recorded in the 400 nm-800 nm wavelength region. Increase in the transmittance is observed with an increase in Mo doping concentration (Table 3). Absorption coefficients for the deposited films are calculated using the relation [17]

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \quad (5)$$

where t is the film thickness and T is the transmittance of the film. The direct bandgap values of the films are obtained using the formula [16]

$$\alpha h\nu = B(h\nu - Eg)^{1/2} \quad (6)$$

where hv is the photon energy, Eg is the optical bandgap and B is aconstant.

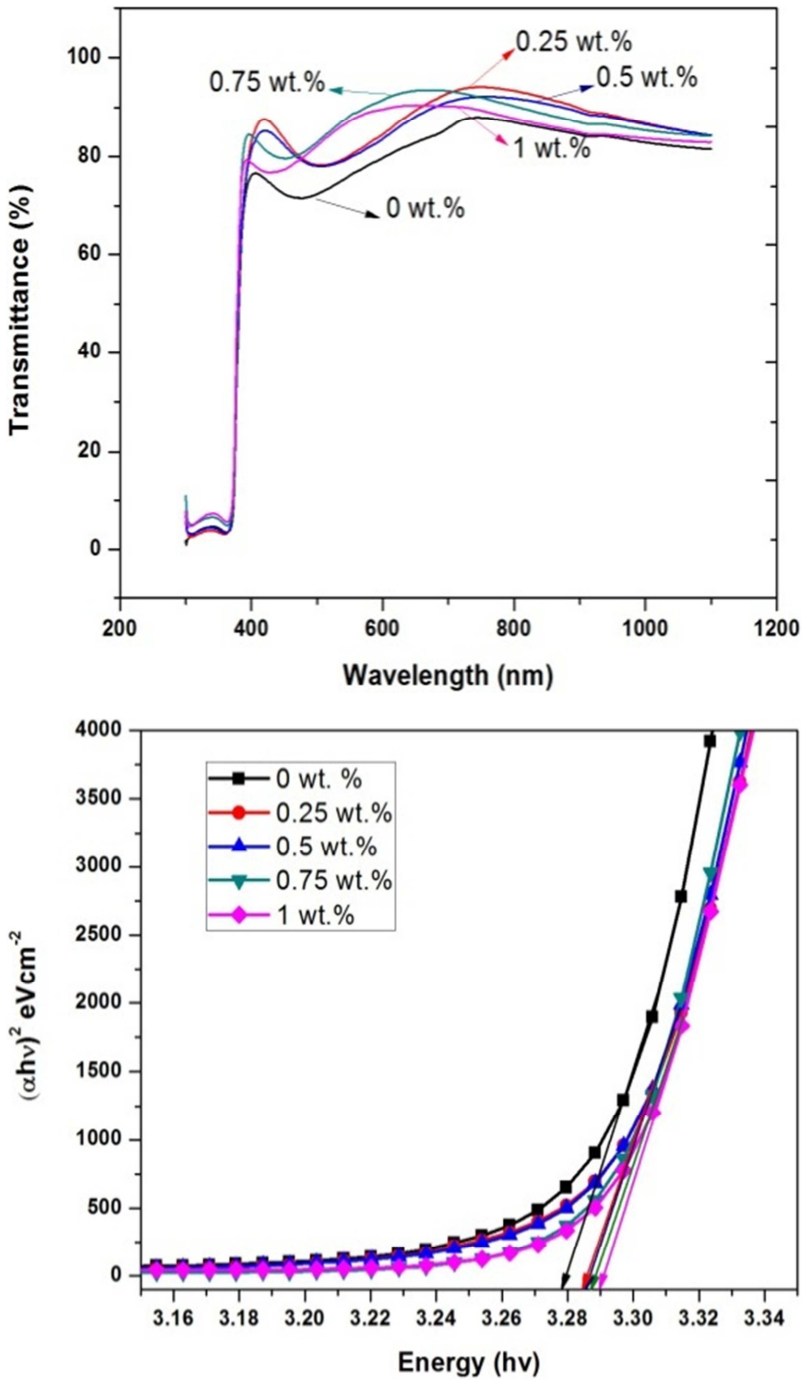

Figure 4. *Optical transmittance spectrum and optical bandgap values of ZnO and Mo:ZnO thin films.*

Table 3. *Average and maximum transmittance, and optical bandgap for ZnO and Mo:ZnO thin films.*

Mo doping Concentration (wt.%)	Average Optical transmittance(%) 380 nm - 800 nm	Maximum Optical transmittance (%)	Optical Bandgap (eV)
0	79.90	88(700 nm)	3.278
0.25	86.66	95(750 nm)	3.285
0.5	85.42	90(750 nm)	3.286
0.75	88.46	94(650 nm)	3.288
1	86.15	89(650 nm)	3.290

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

4. Conclusion

Pure and molybdenum doped zinc oxide thin films were

coated on glass slide at 673K using spray pyrolysis method. XRD patterns 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 1w t.% Mo doping concentration. The biaxial stress values obtained for all the films are found to be compressive in nature. SEM images show the surface with nearly uniform distribution with hexagonal structured grains. RMS roughness values obtained from AFM images show a decreasing trend with increasing Mo doping level. Results from UV-Vis spectra of the films show an average visible transmittance (AVT) of about 88% recorded in the 400-800 nm wavelength region. A slight increase in the bandgap of ZnO is observed with increasing Mo concentration.

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