

Preparation and Characterization of Sprayed Mo-doped ZnO Films

T. Sreenivasulu Reddy*, M. Vasudeva Reddy**, K.T. Ramakrishna Reddy*

* Department of Physics, Sri Venkateswara University, Tirupati, India.

** School of Chemical Engineering, Yeungnam University, Gyeongsan712-749, Republic of Korea.

Abstract- Zinc oxide (ZnO) thin films doped with molybdenum (Mo) have been grown on corning 7059 glass substrates by spray pyrolysis technique. The layers were deposited for different solution concentrations ranging from 0.01M to 0.2M, keeping Mo – doping constant as 2 at. %. The change in properties of the films by varying Zn molarity was studied. X-ray diffraction studies showed polycrystalline nature of the films with (002) preferred orientation and exhibited wurtzite structure. The layers formed at 0.1M molar concentration exhibited better crystallinity compared to other layers. Raman studies are in good agreement with XRD. Surface morphology varied significantly with Zn-molar concentration. An average transmittance of the layers was 80% in the visible region and the band gap varied from 3.31 eV to 3.5 eV. The detailed analysis of the results including photoluminescence are reported and discussed.

Index Terms- Thin films; ZnO: Mo; spray pyrolysis; structural properties; optical properties.

I. INTRODUCTION

Transparent conducting oxide films have been widely studied in recent years. ZnO is the most preferable material over other oxide thin films. Its main advantages are low cost of precursor materials, relatively low deposition temperature, non-toxicity, stability in hydrogen plasma atmosphere [1-3]. Moreover, zinc oxide thin films have been used for various applications, such as solar energy conversion [4, 5], gas sensors [6-7] and light emitting devices [8]. ZnO is an n-type semiconductor with a wide band gap. This can be doped with a wide variety of elements to meet the requirements of the field of application. Preparation of ZnO thin films with dopants like Mg, Al, B, Ga, In, Sn, F, [8-15] by using chemical spray technique was reported by many investigators. In many of these investigations, the authors reported their work using zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) as the precursor for zinc. But, in the present work we used zinc chloride ($ZnCl_2$) as the precursor with Mo-dopant [16]. Molybdenum is the potential dopant material for improving conductivity and transparency of zinc oxide thin films. Mo-doping in ZnO lattice is very beneficial because of a valence difference of 4 between Mo^{6+} and Zn^{2+} , thus enabling each dopant atom of dopant to contribute 4 free electrons to the electrical conductivity. Mo-dopant appears to be very successful because of its smaller ionic radius 0.06nm [17]. Mo-doped ZnO films have been grown using different methods such as RF and DC sputtering [18-19] and the ion beam sputtering deposition [20]. In comparison of the films grown by spray pyrolysis, it is quite simple and the required experimental

set-up is less expensive and flexible for process modification. Furthermore to produce large area films, spray pyrolysis is easily adoptable. There are less investigations on Mo-doped ZnO films by spray pyrolysis method in literature. In this work we report on the growth of Mo-doped ZnO (MZO) films by chemical spray process and the results on film characterization.

II. EXPERIMENTAL

Mo-doped ZnO thin layers were prepared by the spray pyrolysis method on corning 7059 glass substrates at a constant substrate temperature of 400°C. Zinc chloride ($ZnCl_2$, Aldrich 98%) and molybdenum chloride ($MoCl_5$, Aldrich 95%) were used as precursors for of zinc and molybdenum respectively. Methanol was used as solvent for preparation of precursor solutions. The Zn molarity was varied in the range 0.01M - 0.2M, to investigate its effect on the preparation of MZO thin films. The solution was sprayed at a flow rate of 6ml/min and compressed air was used as the carrier gas with a flow rate of 8l/min. A distance of 25cm was maintained between substrate and the nozzle. The solution was sprayed for 15s and paused for 1min to overcome cooling of the substrates. The deposition was carried out using automated stepper motor system to get uniform coating of the film on the substrate. The structural properties were studied using a Siefert X-Ray diffractometer (XRD) with a CuK_{α} radiation source ($\lambda=1.542 \text{ \AA}$). Raman studies were carried out using Horiba Lab Ram HR spectrometer using a laser of wavelength 532nm for excitation. FSI serion scanning electron microscope was used for surface morphology studies. The optical properties were determined using UV-Vis-NIR spectrophotometer (Perkin Elmer lamda –950). The photoluminescence properties of the films was studied by YVON Florolog-3 (model:FL3-22) with xenon flash lamp as source.

III. RESULTS AND DISCUSSIONS

The as-grown MZO films were uniform, pin hole free, pale whitish in appearance and strongly adherent to the substrate surface. The film surface was found to be rough. The X-ray diffraction spectra of MZO films formed using different Zn-concentrations with 2 at. % Mo-doping are shown in fig 1. All the films were polycrystalline in nature and showing a structure with the appearance of (100), (002) and (101) peaks. The crystal structure of the grown films was evaluated to be hexagonal wurtzite. With the increase of solution molarity, the intensity of the (002) peak increased up to the molarity of 0.1M and afterwards it is decreased. When the Zn concentration in the solution was higher than 0.1M, the (102), (103) and (112)

reflections also appeared in the XRD spectra and their intensity increased with increase of Zn-concentration. This might be due to (more amount of) Mo incorporation with increasing molarity, results in disorder. No change in preferred orientation is noticed, this clearly shows the perfect substitutional incorporation of Mo in Zn sites.

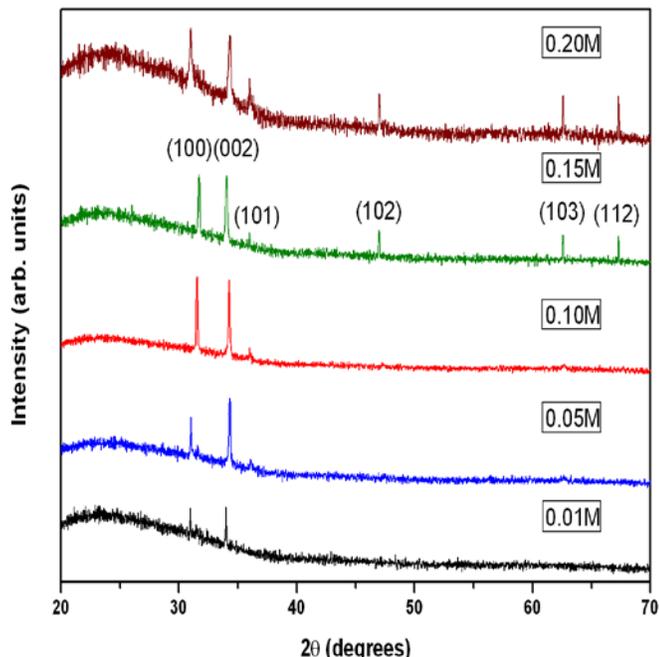


Fig. 1. XRD pattern of MZO films formed at a substrate temperature of 400°C using different Zn- molar concentrations.

The crystallite size (D) of MZO films prepared at different molar concentrations calculated using full width at half maximum (FWHM) for preferred orientation, (002) using Scherrer formula [21],

$$D = \frac{c\lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

where β is the full width at half maximum in radians, θ is diffracting angle and λ is the wavelength of X-rays and C is the correction factor, which is taken as 0.9. Fig.2 shows the change of crystallite size with Zn- molar concentration in the starting solution. As Zn molar concentration increases, the crystallite size also increased up to 0.1M and on further increase of Zn-molarity the crystallite size starts decreasing. The dislocation density (δ) was estimated from the following relation [22],

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

and the variation of dislocation density with Zn-content in the starting solution is shown in fig. 2. It shows a sharp decrease of dislocation density with increase of Zn-molar concentration up to 0.05M and seems stable afterwards. A minimum dislocation density of $2 \times 10^{-8} \text{ \AA}^{-2}$ was observed at 0.1M. This was due to the higher crystallite size observed at this concentration.

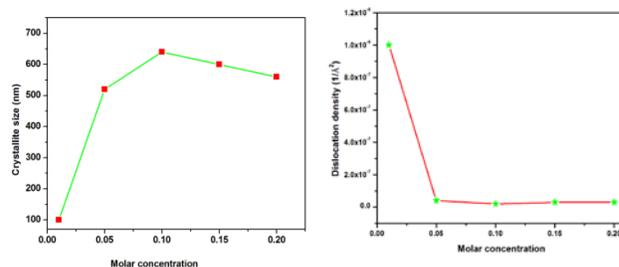


Fig.2. Variation of crystallite size and dislocation density of MZO films.

The lattice parameters, ‘ a ’ and ‘ c ’ were calculated using the relation [21],

$$\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left[\frac{h^2 + hk + k^2}{a^2} \right] + \frac{l^2}{c^2} \dots \dots \dots (3)$$

where d is the inter planar spacing, determined using Bragg’s equation and h, k, l are the Miller indices of the lattice planes. The evaluated lattice parameters for the films grown at 0.1M, Zn-doping were $a = 3.25 \text{ \AA}$ and $c = 5.19 \text{ \AA}$. In order to investigate the vibrational properties of MZO films and the influence of solution concentration on their micro structure, phase and other related parameters, Raman spectra recorded in the range of 150–800 cm^{-1} and are shown in Fig. 3. In general the wurtzite crystal structure of ZnO belongs to C_{6v}^4 space group with two formula unit primitive cells where all the atoms are occupying the C_{3v} sites [23]. According to group theory, the corresponding zone centre optical phonons are of the following symmetry modes: $A_1 + 2B_1 + E_1 + 2E_2$. The $A_1 + E_1 + 2E_2$ modes are Raman active, while $2B_1$ phonons are silent. The A_1 and E_1 modes are split into longitudinal optical (LO) and transverse optical (TO) components [23]. The peak at about 438 cm^{-1} can be assigned to E_2 mode (E_2 high) of ZnO. At low starting solution molarity value the Raman peak related to E_2 mode appears very broad and weak, indicating low crystallinity. This result is in agreement with the XRD data. The peak at about 573 cm^{-1} can be assigned to A_1 longitudinal optical (LO) mode. In the same spectra a weak peak is observed at 342 cm^{-1} , which corresponds to low frequency E_2 second order phonon.

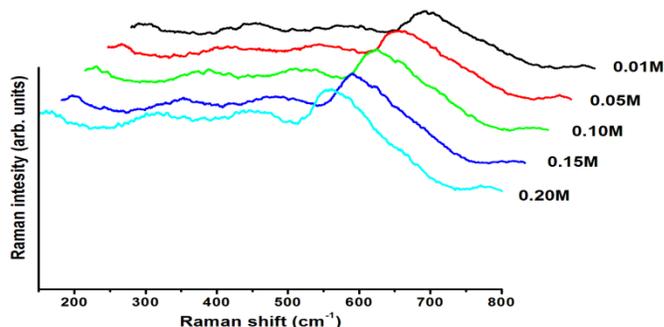


Fig. 3. Raman spectra of MZO films grown with different Zn-molar concentrations.

SEM micrographs of MZO films with different Zn-molar concentrations are shown in fig.4. A clear change in the crystallinity of the films is observed with increase in Zn molarity

in the starting solution. As solution molarity increased, the crystallinity has been increased for the films having molarities up to a value of 0.1M and then decreased for higher molarities. The evaluated grain size of the layers formed with molarity of 0.1M is 650nm. This result is very good in agreement with XRD results.

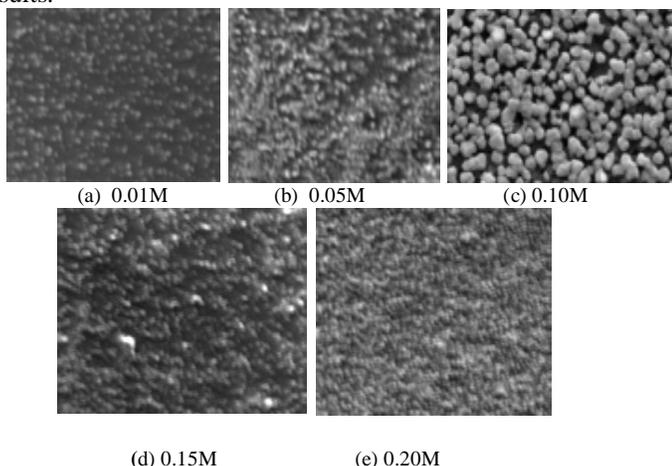


Fig. 4. SEM pictures of MZO films grown with different Zn-molar concentrations.

Fig.5 shows the transmittance versus wavelength plots of the films grown at different starting solution molarities. An average transmittance of 80% was exhibited by all the films. It is clear from the plots that higher molar concentration films showed lower transmittance compared to the layers formed using lower solution molarities. The decrease in transmittance at higher concentration is because of increasing thickness of the film (0.01M-120nm; 0.05M-200nm; 0.1M-340nm; 0.15M-390nm; 0.2M-500nm). Also then high surface roughness of the layers could be the reason for the low transmittance as rough surface increases the light scattering and reduces the transmittance.

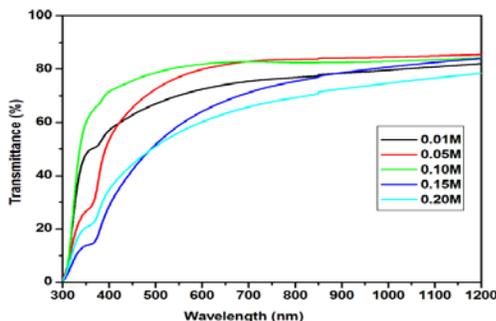


Fig. 5. Optical transmittance versus wavelength spectra of MZO films.

The absorption coefficient, α was calculated using the relation [21],

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \dots \dots \dots (4)$$

where t is the film thickness and T is the transmittance of the film. The dependence of absorption coefficient, α on the photon energy, $h\nu$ gives the information regarding the electronic

transition between the valence band and conduction band in semiconductors. The energy absorbed by the sample for direct/indirect optical transition from the incident photon energy, $h\nu$ is calculated using the relation,

$$ah\nu = A(h\nu - E_g)^m$$

where A is a constant, E_g , the energy band gap, $h\nu$, the incident photon energy and ' m ' is the nature of the optical transition involved between the parabolic bands in the material. Here $m = 1/2$ indicates direct allowed transition; $m = 3/2$ reveals direct forbidden transition, $m = 2$ shows indirect allowed transition and $m = 3$ infers indirect forbidden transition. In this study, the data followed the above relation with $m = 1/2$, indicating the presence of direct allowed transition in the layers. Fig.6 shows the variation of energy band gap with molar concentration of the starting solution. The band gap varied from 3.31eV to 3.5eV and the observed values are in agreement with the literature values [24].

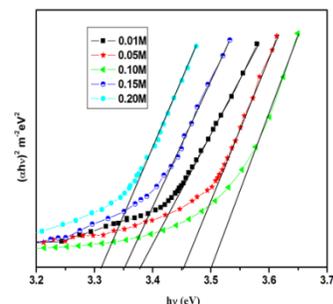


Fig. 6. $(ah\nu)^2$ versus $h\nu$ plots of MZO films.

Fig.7 gives the comparison of photoluminescence spectra of MZO films prepared with different starting solution molarities. A strong peak was noticed at wavelengths between 360nm and 390nm that corresponds to the energy band gap of the layers. With the increase of solution molarity in the ZnO crystal lattice, the intensity of the peak centered at 410nm gradually increased and the peak became strong. This is in good agreement with the optical data observed in the study, which confirms that optical behaviour of Mo-doped ZnO layers was increasing with solution molarity. Further, a low intensity broad peak was observed at 525nm that was related to green emission, which originates from the oxygen vacancies.

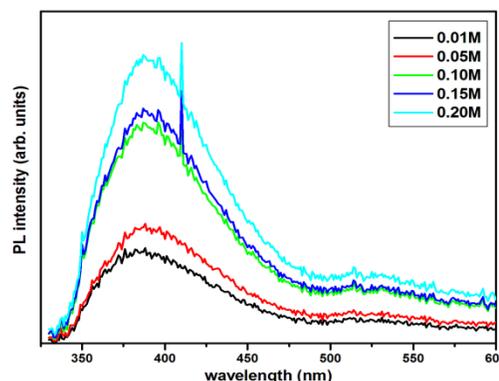


Fig. 7. Photoluminescence spectra of MZO films grown with different precursor concentrations.

IV. CONCLUSION

ZnO thin films with different Mo-doping concentrations have been prepared at a substrate temperature of 400°C. The X-ray diffraction studies showed good crystallinity at 0.1M molar concentration that showed a strong (002) plane as preferred orientation. The Raman studies revealed only ZnO phase. The morphological studies indicated better grain size of 650nm for the films formed at 0.1M molar concentration. The optical results identified that films with 0.1M concentration showed optical transmittance of 80% in the visible region and the energy band gap varied between 3.31eV to 3.5eV. The photoluminescence data supported the change in band gap with solution concentration. These crystalline, single phase and transmissive Mo-doped ZnO layers could be used as window layers in solar cells.

Acknowledgement

The authors would like to thank Dr.N.Revathi and Prof.E.Mellikov, Dept of materials science, Tallin Technical university, Estonia for XRD and Raman analysis.

REFERENCES

- [1] Z.C.Jin, J.Hamberg, C.G.Granquist, J.Appl.Phys., Vol. 64, 5117, 1988.
- [2] J.B.Yoo, A.LFahrenbruch, R.H.Bube, J.Appl.Phys., Vol. 68, 4694, 1990.
- [3] S.Major, S.Kumar, M.Bhatnagar, K.L.Chopra, Appl.phys.lett., Vol. 49, pp 394-396, 1986.
- [4] J.I.Oda, J. I.Nomoto, T.Miyata, T.Minami, Thin solid films, Vol. 11, pp 2984-2987, 2010.
- [5] D.R.Sahu, Shin-Yuan Lin, Jow-Lay Huang, Applied surface science, Vol. 252, pp 7509-7514, 2006.
- [6] V.M.Arakelyan, V.E.galstyan, G.E. Shahnazaryan, Armenian Journal of physics, Vol. 1, pp 138-141, 2008.
- [7] J.F.chang, H.H.Kuo, I.C.Leu, M.H.Hon, Sensors and Actuators B., Vol. 84 pp 258-264, 2002.
- [8] A. Osinsky, J.W. Dong, M.Z. Kouser, B. Hertog, A.M. Dabiran, P.P. Chow, S.J. Peorton, O. Lopatiuk, L. Chernyak, Appl. Phys. Lett., Vol. 85, 4272, 2004.
- [9] A. El Hichou, M. Addou, A. Bougrine, R. Dounia, J. Ebothe, M.

- Troyon, M. Amrani, Materials Chemistry and Physics, Vol. 83, pp 43-47, 2004.
- [10] H. Kim, C.M. Gilmogre, J.S. Harwitz, A. Pique, H. Murata, G.P. Kushto, R. Schlaf, Z.H. Kafafi, D.B. Chrisey, Appl. Phys. Lett., Vol. 76, pp 259-261. 2000.
- [11] R.L. Hoffman, B.J. Narris, J.F. Wager, Appl. Phys. Lett., Vol. 82, pp 733-735, 2003.
- [12] B. Kotlyarchuk, V. Savchuk, M. Oszwaldowski, Cryst. Res. Technol., Vol. 40, pp 1118-1123, 2005.
- [13] J.H. Morgen, D.E. Brodie, Can. J. Phys., Vol. 60, pp 1387-1390, 1982.
- [14] T. Ikuno, R. Suzuki, K. Kitazumi, N. Takahashi, N. Kato, and K. Higuchi, Appl. Phys. Lett., Vol. 102, pp 193901-1 - 193901-4, 2013.
- [15] Y.Caglar, S.Aksoy, S.Ilican, M.Caglar, Superlattices and Microstructures, Vol. 46, pp 469-475, 2009.
- [16] A. El Hichou, M. Addou, J. Ebothe, M. Troyon, Journal of Luminescence., Vol. 113, pp 183-190, 2005.
- [17] Ji- Yun Chun, Jin-Woo Han, and Doue – Shik Seo, electrochem.Solid-state Letters., Vol. 12, pp J47-J49, 2009.
- [18] X. Xiu, Z. Pang, M. Lv, Y. Dai, L. Ye, S. Han, Applied Surface Science., Vol. 253, pp 3345-3348, 2007.
- [19] J.L Shi, H.Ma, G.H.Ma, J.Shen, Appl.phys.A., Vol. 92, pp 357-360, 2008.
- [20] C.C.Kuo, C.C.Liu, S.C.He, J.T.chang, J.L.He, vacuum., Vol. 85, pp 961-967, 2011.
- [21] V. Gokulakrishnan, S. Parthiban, K. Jaganathan, K.Ramamurthi, Ferroelectrics., Vol. 423, pp 126-134, 2011.
- [22] G.B. Williamson, R.C. Smallman, Phil. Mag., Vol. 1, pp 34-45, 1956.
- [23] T. C. Damen, S. P. S. Porto and B. Tell, Phys. Rev., 1966, 142, 570.
- [24] M.A. Lucio-Lopez, M.A. Luna-Arias, A. Maldonado, M. de la L. Olvera, D.R. Acosta, Solar Energy Materials & Solar Cells, Vol. 90, pp 733-741. 2006.

AUTHORS

First Author – T. Sreenivasulu Reddy, Department of Physics, Sri Venkateswara University, Tirupati, Andhrapradesh State, India. E-mail; sreenur8@gmail.com
Second Author – M. Vasudeva Reddy, School of Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea. E-mail; mvrshilpa@gmail.com
Correspondence Author – K.T. Ramakrishna Reddy, Dept. of Physics, Sri Venkateswara University, Tirupati, Andhrapradesh State, India. E-mail; ktrkreddy@gmail.com