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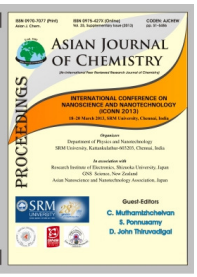

A Comparative Study on Pure and Mg Doped ZnO Nano Structured Thin Films†

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Pure and Mg doped zinc oxide thin films were prepared on glass substrates by chemical bath deposition method. These films were characterized for their structural, morphological, optical and functional properties by means of powder X-ray diffraction, scanning electron microscopy, UV-visible spectroscopy and Raman analysis. Powder XRD results showed that ZnO nano crystallites have hexagonal structural phase. SEM micrographs revealed homogeneous flower shaped structures for pure ZnO thin films and flower petals were bound to the spherical shape for the case of Mg doped ZnO. Optical and functional properties of the films were studied from UV-visible and Raman analyses respectively.

Key Words: ZnO thinfilms, Optical properties, Raman analysis.

INTRODUCTION

Recently, many researchers gained the interest to study transparent zinc oxide, because of its potential multifunctional applications ranging from transparent electrodes in solar cells, thin film gas sensors, light emitting diodes, photo detectors and spintronic devices based on its wide direct band gap (~3.3 eV) and large exciton binding energy (~60 meV) at room temperature[1]. A variety of novel nanostructured ZnO materials including nanowires, nanobelts, nanorods, nanocombs, nanosheets, tetrapods, feather-like and flower-like have been reported[2]. Zinc oxide based films have been deposited on various substrates by different methods like sputtering[3], pulsed laser[4], chemical bath deposition[5], spray pyrolysis[6], chemical vapour deposition[7], vapour transport deposition[8] and sol-gel process[9]. The ZnO with Mg doped thinfilm are shown to realize the control of the band gap for the operation of light-emitting devices in a wider wavelength region[10] without affecting the lattice, because of similar ionic radius of Mg (0.57 Å) and Zn (0.60 Å)[11], the Zn positions can be easily substituted by Mg under certain conditions. In the present work, pure and Mg doped ZnO thin films have been coated on the glass substrate by chemical bath deposition method. The structural, morphology and optical properties of ZnO and Mg doped ZnO thin films are carefully investigated.

EXPERIMENTAL

Commercially available glass (microscope slides) was used as a substrate. Before the deposition, the glass slides were cleaned by chromic acid solution for 12 h at 90 ºC, washed with distilled water for several times and finally dried at room temperature. Zinc acetate dihydrate, magnesium chloride and sodium hydroxide (NaOH) of analytical reagent grade were purchased from Merck chemical company. For the preparation of pure ZnO thin film, precursor solution was prepared from 0.1 M zinc acetate and 0.2 M sodium hydroxide and then mixed in de-ionized water with continuous stirring. Ammonia was added into the solution to maintain the pH around 8 ± 0.2. A cleaned substrate was immersed in the precursor solution at 80 ºC for 1 h. Finally ZnO has uniformly deposited on the glass substrate in the area beneath the solution. After the deposition the film was rinsed with distilled water and dried in air. Magnesium doping was carried out by adding 3 wt % of $MgCl_2$ into the main precursor solution and the above deposition procedure was carried out for preparing Mg doped ZnO thin film.

RESULTS AND DISCUSSION

Structural analysis: The structural information about the pure and Mg doped ZnO thin films have been obtained by powder XRD. The position of all peaks are indexed and all have well coincidence with the standard pattern (JCPDS No: 792205) shown in Fig. 1. The comparison of pure and Mg doped thinfilm formation implies that both thin films have a hexagonal structure. The sharp and intense peaks indicate that both pure and Mg doped ZnO thin films are highly crystalline

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TABLE-1
MICROSTRUCTURAL AND LATTICE PARAMETERS OF PURE AND Mg DOPED ZnO THINFILMS

Samples	Crystallite size (nm)	Lattice parameter		c/a ratio	u-Parameter	Cell volume
		a (Å)	c (Å)			
Pure ZnO	48.847	3.253	5.208	1.6009	0.3800	47.726
Mg doped ZnO	29.420	3.251	5.207	1.6017	0.2933	47.658

and uniformly coated thin films have polycrystalline nature. The XRD peaks for (100), (002) and (101) planes indicates the formation of pure hexagonal structure of ZnO phase. Comparing the intensity of the XRD patterns, we note that peak intensities are increasing for Mg-doped ZnO thinfilms, which infer that dopant enhance the crystallinity. This phenomenon is found for many doped metal oxides[12].

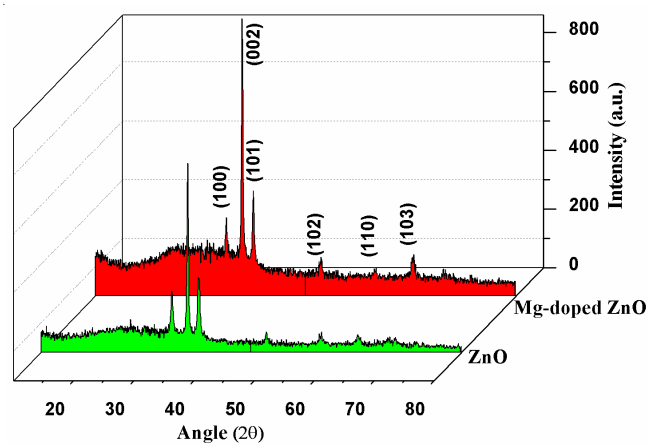

Fig. 1. XRD spectrum of pure and Mg doped ZnO thin films

Furthermore, from the powder XRD data, microstructural parameters like lattice parameter, crystallite size, u-parameter and cell volume were calculated for the pure and Mg doped ZnO thinfilms. Table-1 shows the calculated microstructural parameters for pure and Mg doped ZnO thinfilms. The crystallite size was decreased for Mg doped ZnO thin films compared to pure one. These structures have two interpenetrating sublattices in which two constituent atoms are displaced by each other by a value of 'u'.

Here the u parameter is calculated by:

$$u = \left(\frac{a^2}{3c^2}\right) - 0.25 \rightarrow \langle 1 \rangle$$

Morphological and compositional analysis: The micrographs of the pure and Mg doped ZnO thinfilms have been investigated by SEM and the corresponding results are shown in Fig. 2. For pure ZnO thin film, flower shaped structures was observed. For Mg doped ZnO thinfilms, the same flower shaped formation was obtained but the patels were bounded to spherical shape due to the addition of Mg.

EDS analysis was carried out to identify the elemental composition of pure and Mg doped ZnO thin films and corresponding results are shown in the inset of Fig. 2. The ZnO thin film was composed of Zn and O atoms and their atomic percentages are 59.14, 40.86 respectively. Mg doped ZnO thinfilm was composed of Zn, O and Mg atoms and their atomic percentages are 46.89, 51.59 and 1.52 respectively. This result reveals that the material is composed of expected elements and their atomic percentages are nearly stoichiometric ratio. The presence of Mg is also identified from the spectrum.

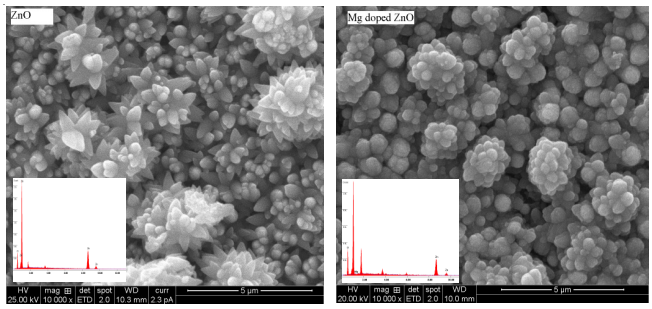

Fig. 2. SEM with EDS images of pure and Mg doped ZnO thin films

Optical analysis: In order to investigate the optical property of the deposited thin films, UV absorption spectrum was taken for pure and Mg doped ZnO thin films. The optical absorption coefficient α, was evaluated from absorption spectrum using the following equation, $\alpha = 1/t\ (\ln A)$, where t is the thickness of the film obtained and A is the absorption. The coefficient α varies with photon energy hν. E_g is the optical band gap for allowed direct band transition. Fig. 3 shows the plot of $(\alpha h\nu)^2$ *versus* photon energy hν of the pure and Mg doped ZnO thin films. The optical band gap values were determined by extrapolating the linear portion of the Tauc plots to intersect the energy axis. The optical band gap of the films decreased from 3.3 to 3.2 eV because of doping effect of magnesium. This narrowing band gap is due to improved crystallinity and decreased grain size of the thin film.

Functional analysis: The Raman spectrum is used to identify the crystal quality, structural defects and disorder formation of the film. ZnO has the hexagonal wurtzite structure that belongs to C_{6v} symmetry group. The Fig. 4 shows the Raman

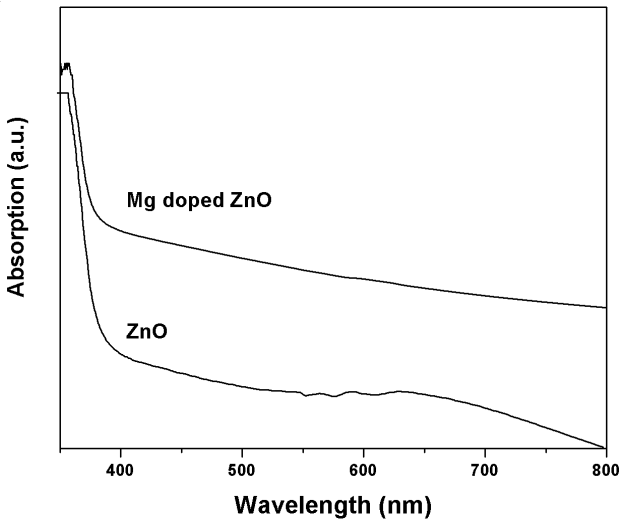

Fig. 3(a) Optical absorption spectrum for pure and Mg doped ZnO thin film

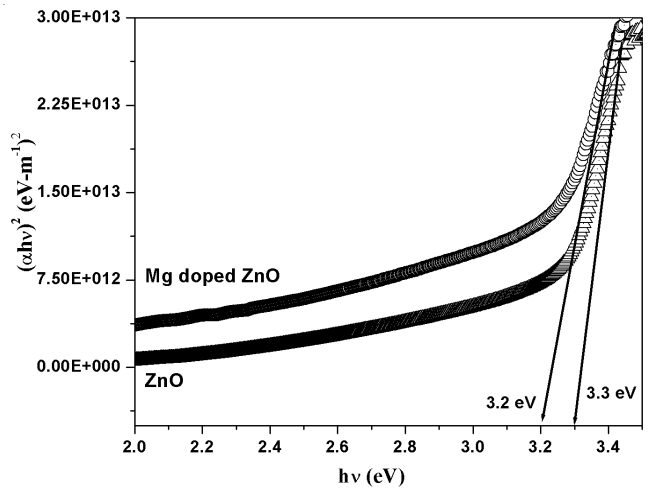

Fig. 3(b). Tauc plot for pure and Mg doped ZnO thin film

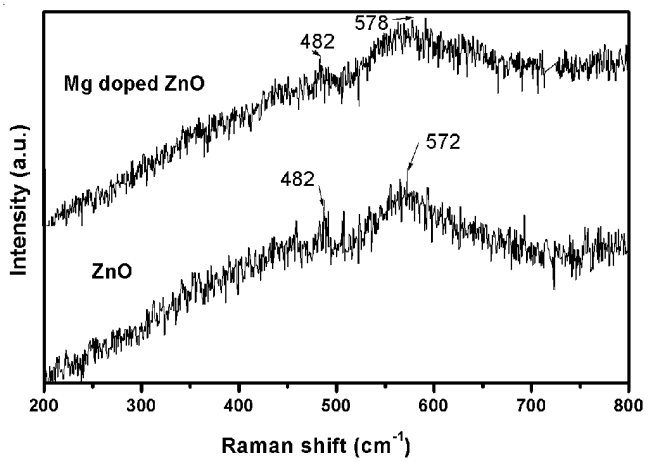

Fig. 4. Raman spectra of pure and Mg doped ZnO thin films

spectra of pure and Mg doped ZnO thin films. Small changes could be observed in the Raman spectrum of Mg doped ZnO in comparison with the spectrum of pure ZnO thin film. The mode 482 cm^{-1} is related to the vibration of oxygen atom in ZnO hexagonal wurtzite structure. Another intense peak is identified in the spectrum which corresponds to the longitudinal optical mode which shifts from 572 to 578 cm^{-1} for Mg doped ZnO. Comparing the pure and doped thin films, the Mg doped ZnO film have shown the shifting of longitudinal optical modes to the higher frequency side and this may be due to substitution of Mg in Zn position.

Conclusion

Pure and Mg doped ZnO thin films have been successfully deposited on the glass substrates by chemical bath method. The powder XRD pattern indicated that pure and Mg doped ZnO thin films have hexagonal structure and no secondary phase was detected which indicated that Mg ions are substituted in ZnO lattice. The flower shaped structures of pure ZnO thin films was converted into spherical shaped one for the Mg doped ZnO observed from SEM photographs. The presence of Mg in the doped thin film was conformed from the EDS analysis. The optical absorption studies have been used to compare the optical properties of Mg doped ZnO thin film with pure ZnO. The band gap of Mg doped ZnO (3.2 eV) was blue shifted compared to pure ZnO band gap (3.3 eV). This is due to the effect of dopant material substituted at Zn^{2+} sites of ZnO. The results of Raman spectrum ascertain that the longitudinal optical mode of Mg doped ZnO was shifted to higher frequency side compared to pure ZnO thin film.

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REFERENCES

1. R. Ding, C.X. Xu, B.X. Gu, Z.L. Shi and H.T. Wang, *J. Mater. Sci. Technol.*, **26**, 601 (2010).
2. S.G. Hussain, D.M. Liu, X.T. Huang and S. Ali, *J. Phys. Chem. C*, **112**, 11162 (2008).
3. S.H. Choi and J.S. Kim, *Ultramicroscopy*, **108**, 1288 (2008).
4. H. Yu and W. Zhang, *Mater. Lett.*, **62**, 4263 (2008).
5. T. Mazingue, L. Escoubas, L. Spalluto, F. Flory, G. Socol, C. Ristoscu, E. Axente, S. Grigorescu, I.N. Mihailescu and N.A. Vainos, *J. Appl. Phys.*, **98**, 074312 (2005).
6. N. Kavasoglu and A.S. Kavasoglu, *Physica B*, **403**, 3159 (2008).
7. J. Hu and R.G. Gordon, *J. Appl. Phys.*, **71**, 880 (1992).
8. H.J. Fan, B. Fuhrmann, R. Scholz, C. Himcinschi, A. Berger and H. Leipner, *Nanotechnology*, **17**, 231 (2006).
9. P.T. Hsieh, Y.C. Chen, K.S. Kao, M.S. Lee and C.C. Cheng, *J. Eur. Ceram. Soc.*, **27**, 3815 (2007).
10. G. Wang, Z.Z. Ye, H.P. He, H.P. Tang and J.S. Li, *J. Phys. D, Appl. Phys.*, **40**, 5287 (2007).
11. E. Diler, S. Rioual, B. Lescop, D. Thierry and B. Rouvellou, *Thin Solid Films*, **520**, 2819 (2012).
12. S.B. Ogale, R.J. Choudhary, J.P. Buban, S.E. Lofland, S.R. Shinde, S.N. Kale, V.N. Kulkarni, J. Higgins, C. Lanci, J.R. Simpson, N.D. Browning, S.D. Sarma, H.D. Drew, R.L. Greene and T. Venkatesan, *J. Phys. Rev. Lett.*, **91**, 077205 (2003).