Exp. Theo. NANOTECHNOLOGY 8 (2024) 17-22 https://doi.org/10.56053/8.1.17

Structural investigations of ZnO nanostructure

J. G. Kim[*], *P. Tan*

Department of Materials Science, Pohang University of Science and Technology, Pohang 790-784, Korea
[*]) Email: kimjg@postech.ac.kr

Received 23/8/2023, *Accepted* 4/12/2023, *Published* 15/1/2024

Undoped and Mn-doped ZnO samples with different percentages of Mn content (1, 5 and 10 at%) were synthesized by a dip coating sol–gel method. We have studied the structural, chemical and optical properties of the samples by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-visible spectroscopy. The XRDspectra show that all the samples are hexagonal wurtzite structures. We note that doping favors *c*-axis orientation along (002) planes. Up to 5 at% of Mn doping level, the *c*- axis lattice parameter shifts towards higher values with the increase of manganese content in the films. The expansion of the lattice constant of ZnO–Mn indicates that Mn is reallydoped into the ZnO. The SEM investigations of all samplesrevealed that the crystallites are of nanometer size. The sur-face quality of the ZnO–Mn film increases with Mn dopingbut no significant change of the grain size is observed from SEM images. The transmittance spectra show that the transparency of all the samples is greater than 85 %. We note, also, that a small doping (1 %) lowered the refractive index while the thickness of the layers and the gap increase. However, on raising the proportion of Mn beyond 5 %, practically the same values of index and gap as pure ZnO are found.

Keywords: Cu_2CdSnS_4; Nanostructures; Optical; Structural; Electrical.

1. INTRODUCTION

Semiconductor nanostructures are of great interest for their well-known performance in electronics, optics and photonics. Zinc oxide, a member of the II–VI group with a wide band gap (3.31 eV) and a large excitonic binding energy(60 meV) [1, 2], has been used in a wide range of device ap-plications due to its semiconducting, optical, electrical andpiezoelectric properties [3, 4]. ZnO is a good candidate asoptoelectronic device material for use in the blue and violetregions. Good *c*-axis-orientated crystalline structure is desirable for applications where crystallographic anisotropy isneeded such as piezoelectric surface acoustic wave devices.Diverse other properties such as optical transparency in thevisible region, high voltage–current nonlinearity, chemical stability, biocompatibility, etc., impose ZnO material in different applications like short-wavelength light-emitting de-vices, transparent electrodes, gas sensors and solar cells [5].Transition-metal-doped ZnO has the potential to be a multifunctional material with

coexisting optical, semi con-ducting and magnetic properties. The interest in doping ZnOis to explore the possibility of improving these characteristics. The doping of transition-metal elements into ZnO allows the creation of sub energy levels in the band gap to make use of it as UV detectors and light emitters. It has been reported that the band gap reduces for low-concentration doping (3 at%) and increases for higher concentration [6]. For the low-concentration Mn doping, the reduction in the band gap has been theoretically explained as a consequence of exchange interaction between the d electrons of the transition-metal ions (Mn) and the s and p electrons of the host band. For the higher concentration (>3 mol%) Mn doping, the augmentation is due to the large band gap of MnO (4.2 eV) [7].
There are many reports in the literature describing the preparation of ZnO thin films by a variety of techniques, including pulsed laser deposition, RF magnetron sputtering, chemical vapor deposition (CVD), molecular beam epitaxy (MBE), spray pyrolysis [8], etc. The sol–gel process is simple, inexpensive and has the advantage of uniformity of deposited film thickness and, also, a large-area deposition. Sol–gel thin-film deposition is a good alternate way to obtain a particle size of less than 20 nm and provides excellent control of composition.
So far, it has been much reported that ZnO was doped with In, Al, Ga, P, N, Li and Mg for electrical and optical applications. Some papers on ZnO films with Mn2+ doping concentrating on ferromagnetic properties have been re- ported, too. However, there are not many reports about ZnO films doped with Mn^{2+} applied for piezoelectric devices. The goal of this work is to synthesize Mn-doped samples using sol–gel dip coating and to analyze the effect of doping on structural, surface morphology and optical properties of nano thin films.

2. EXPERIMENTAL

Mn-doped ZnO thin films were obtained by a sol–gel process. Zinc acetate, ethanol and diethanolamine (DEA) are respectively used as precursor, solvent and stabilizer. Manganese acetate was used as source of doping. ZnO sol was obtained by dissolving zinc acetate 0.6 M under stirring at 50 °C in a solution of ethanol and DEA for 1 h. Mn- doped ZnO sol was obtained by adding zinc acetate and manganese acetate simultaneously to the solution of ethanol and DEA. A dip coater (KSV) apparatus was used for de- positing thin layers on glass substrates with a withdrawal rate of 20 mm/min. After each deposition, the as-deposited films were dried at 150 °C for 40 min. The operation was repeated to produce three layers. Then the samples obtained were calcined at the temperature of 550 °C. Three sets of samples with different Mn doping levels (1 at%, 2 at% and 3 at%) were obtained.
The thin films prepared were characterized by X-ray diffraction (XRD) at grazing incidence using a PanAnalytical diffractometer. X-rays are produced from a CuK radiation source (wavelength 1.54 Å), an acceleration voltage of 40 kV and a current of 30 mA. The SEM images were obtained by a Zeiss scanning electron microscope. The optical transmittance spectra were obtained using a Jobin-Yvon HR460 UV-visible spectrometer.

3. RESULTS AND DISCUSSION

Reflection versus wavelength was conducted using UV-vis spectroscopy at the range, 200-1000 nm. In agreement with Tauc equation [9] for determining the optical band gap, that can be determined; Figure 1 shows the XRD patterns of the undoped and dopedZnO:Mn films. All the peaks of the XRD patterns are indexed to ZnO with the hexagonal wurtzite structure. We note that doping favors orientation along (002) planes. There is also a reduction in the intensity of the (100) peak with increasing Mn concentration. Small peak broadening occurs with an increase of the manganese content. This indicates that the crystallite grain size increases with an increase of Mn percentage in the films (Table 1).

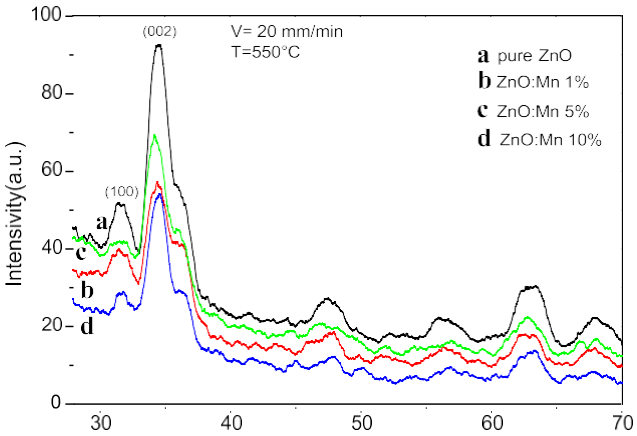

Figure 1 X-ray diffraction spectra of the ZnO and ZnO:Mn films.

Table 1 Average grain size of as-deposited films (002 peaks) for different concentrations.

Mn–ZnO doping level (at%)	Grain size (nm)
0	18.2
1	14.5
5	17.1

Figure 2 shows a SEM image of a ZnO–Mn film. The SEM investigations of all samples revealed that the crystallites are of nanometer size. The surface quality of the ZnO– Mn film increases with Mn doping but no significant change of the grain size is observed from SEM images. The optical transmittance spectra of pure ZnO and ZnO– Mn doped at 1 at%, 5 % and 10 at% are shown in Fig. 3. Be- tween 340 and 450 nm the transmittance increases abruptly and then stabilizes slightly above 80 %. The increase of Mn concentration did not shift the edge of the transmittance. Only a low Mn doping (1 %) significantly increases the transmittance between 400 and 500 nm. Elsewhere, the transmittance is almost unchanged. We note the presence of two minima around 520 nm. We note that a small doping (1 %) lowered the refractive index while the thickness of the layers and the gap (Fig. 4) increases. However, raising the proportion of Mn beyond 5 %, practically the same values of index and gap than pure ZnO are found. Only the thickness of layers increases.

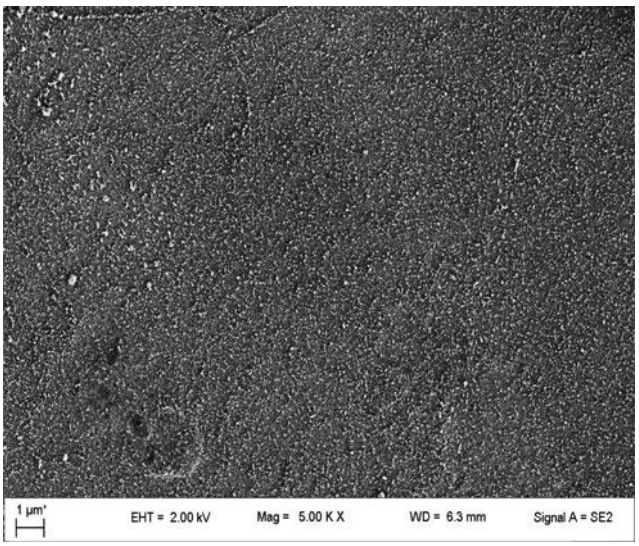

Figure 2 SEM micrograph of ZnO–Mn 5 at%.

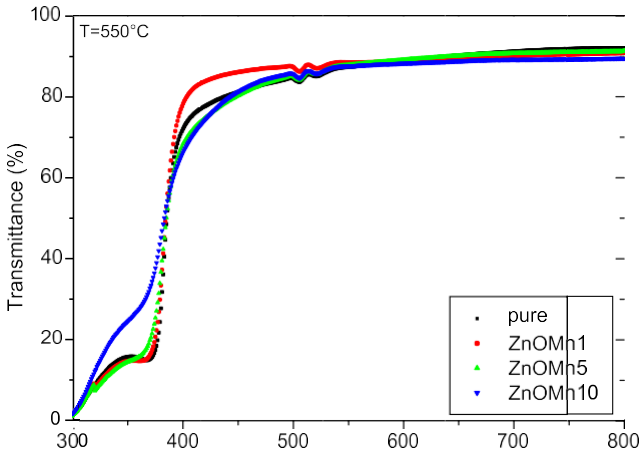

Figure 3 The transmittance spectra of ZnO and ZnO–Mn films.

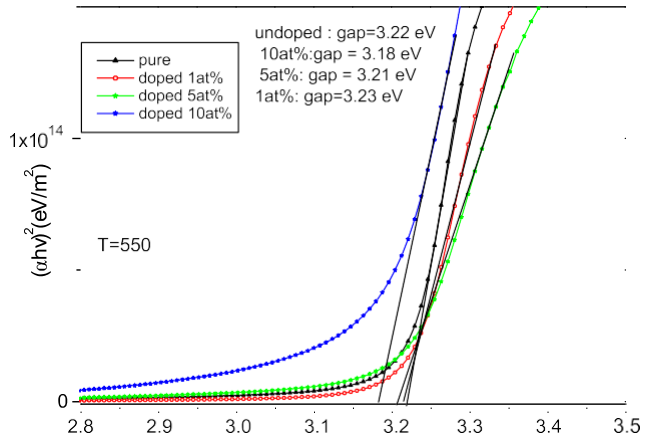

Figure 4 The plot of $(\alpha h\upsilon)^2$ vs. photon energy.

4. CONCLUSIONS

The structural and optical properties of ZnO and ZnO–Mn films prepared by the sol–gel method was studied. The films exhibited a monocrystalline structure with hexagonal wurtzite. While the Mn incorporation deteriorated the crystalline structure of the ZnO film, the surface morphology of the ZnO film enhanced. We note that doping favors c- axis orientation along (002) planes. Optical parameters were calculated and showed that the refractive index dispersion mechanism of both the ZnO and ZnO–Mn films obeys the single-oscillator model. The increase of Mn concentration did not shift the edge of the transmittance. Only a low Mn doping (1 %) significantly increases the transmittance be- tween 400 and 500 nm. Elsewhere, the transmittance is al- most unchanged. Optical band gap energy measurements showed the reduction in the band gap just for 1 at% Mn.

References

[1] X.B. Yu, L.H. Mao, F. Zhang, L.Z. Yang, S.P. Yang, Mater. Lett. 58, 3661 (2004)
[2] R. Viswanatha, S. Sapra, S. Gupta, B. Satpati, P.V. Satyam, V. Dev, Phys. Chem. B 108, 6303 (2004)
[3] J.B. Lee, M.H. Lee, C.K. Park, J.S. Park, Thin Solid Films 447, 296 (2004)
[4] L. Needs, K. Willams, Exp. Theo. NANOTECHNOLOGY 4 (2020) 93
[5] A. M. Ahmed Alwaise, M. Ibrahim Alwiase, A. Y. Qasim, Exp. Theo. NANOTECHNOLOGY 4 (2020) 99
[6] X.T. Zhang, Y.C. Liu, J.Y. Zhang et al., J. Cryst. Growth 254, 80 (2003)
[7] E. Rzepka, G. Berrerar, D. Ferrand, O. Gorochov, Appl. Phys. A 88, 167 (2007)
[8] I. Akyuz, S. Kose, F. Atay, V. Bilgin, Semicond. Sci. Technol. 21, 1620 (2006)
[9] F. Y. Liu, D. Z-H. Tong, L. L. Tian, Exp. Theo. NANOTECHNOLOGY 4 (2020) 115