

Mg-doped ZnO Films by Sol-Gel Spin Coating Method

Derya Peker (Corresponding author)

Department of Physics, Eskisehir Osmangazi University,
Eskisehir 26480, Turkey, dpeker@ogu.edu.tr

Sinan Temel

Central Research Laboratory, Bilecik Seyh Edebali University
Bilecik 11210, Turkey

Murat Nebi

Department of Physics, Eskisehir Osmangazi University,
Eskisehir 26480, Turkey

Abstract

Undoped and Mg doped ZnO films were deposited on glass substrate by sol-gel spin coating method. This method is a simple, economic and effective method to produce high quality films. Structural, morphological and optical properties of films were investigated by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-Visible Spectroscopy respectively. The structure, surface morphology, optical transmittance and band gap were found to depend on the Mg content of the film. XRD results showed that the films were polycrystalline nature and FESEM images proved that the films were homogenous and compact. It was observed that the band gap increases with Mg doping.

Keywords: Sol-Gel method, ZnO, Mg, Films

1. Introduction

Zinc oxide (ZnO) with an energy band gap of 3.3 eV (Bhattacharya et al. 2004) and a large exciton binding energy of 60 meV (Caglar et al. 2010) is one of the most important materials of II-VI semiconductors. ZnO is widely used wide range of technological applications. Examples are solar cells (Minemoto et al. 2000), light emitting diodes (Saito et al. 2002), photodetectors (Liang et al. 2001), etc. Mg doped ZnO films formed by alloying ZnO with MgO showed that the band gap energy varies with the Mg concentration (Cho et al. 2011) By doping ZnO with Mg the bang gap of MgZnO alloys can be tuned from 3.3 to 4 eV (Ohtomo et al. 1998). Due to the ionic radius of Mg^{2+} and Zn^{2+} are similar, the substitution of Zn by Mg does not cause significant changes in lattice structure (Caglar et al. 2010). MgZnO films with wide optical band gap characteristic has several advantages for electro-optical application such as layer of light emitting diodes (LEDs), buffer and TCO layers for thin film solar cells (TFSCs) devices (Kaushal et al. 2009 and Shimakawa et al. 2008). MgZnO alloys are an excellent material system for potential application to exciton-related photonic devices in the UV region (Wang et al. 2008). MgZnO films can be prepared by several methods like as RF Magnetron Sputtering (Minemoto et al. 2000), pulsed laser deposition (Shrama et al. 1999), ultrasonic spray pyrolysis (Zhang et al. 2005), sol-gel method (Moon et al. 2013), etc.

In this study undoped and Mg doped ZnO films were deposited by sol-gel spin coating method. Structural and optical properties and surface morphologies of the films were investigated.

2. Experimental Details

The undoped and Mg doped ZnO films were deposited on glass substrate by sol-gel spin coating method. Zinc acetate dihydrate for ZnO and magnesium acetate tetrahydrate for Mg doping, were used as the starting precursors. 2-methoxyethanol and monoethanolamine (MEA) were used as solvent and stabilizer respectively. The concentration of solutions was 0.5 M and the concentration of Mg doping was 25%. The resultant solution was stirred at 60°C for an hour on a magnetic hot plate. After preparing solutions, undoped ZnO solution was dropped onto glass substrate which were rotated 3000 rpm for 30 seconds and Mg doped solution was dropped onto glass substrate which were rotated 3500 rpm for 30 seconds using spin coater. Both films were dried at 300°C for 10 minutes. This process was repeated for 9 times and then the films were annealed at 500°C in air for 2 hours and then their some physical properties were compared.

3. Results and discussion

3.1 Structural and morphological properties

The crystal structure and the preferred crystal orientation of the undoped and Mg doped ZnO films were investigated by X-ray diffraction (XRD) measurements. XRD measurements were performed by Panalytical Emprayan X-ray diffractometer using $\text{CuK}\alpha$ ($\lambda=1.5405 \text{ \AA}$) radiation in the 2θ range 30°- 80° with a scanning speed of 2°/min. The diffractometer reflection of the films was taken at the room temperature. An X-ray tube operated at 45 kV and 40 mA. Fig.1 shows XRD patterns of the undoped and Fig.2 shows XRD patterns of the Mg doped ZnO films on glass substrate, annealed at 500°C in air for two hours. XRD patterns of the undoped and Mg doped ZnO films were compared in Fig. 3. The indexing of the pattern is according to hexagonal (wurtzite) ZnO and cubic MgO. The diffraction peaks of hexagonal ZnO and those associated with cubic MgO are indexed on the bases of ICDD (International Centre for Diffraction Data): 98-003-1052 and ICDD: 98-064-2712 respectively. XRD spectra for undoped and Mg doped ZnO films indicated that the films are of polycrystalline nature. As it is seen in the Fig. 2 Mg doped ZnO film shows a different (002) MgO peak, which shows that these films generate the segregation phase structure. The surface morphology of the films was studied by FESEM (Zeiss Supra 40VP). Fig. 4 shows FESEM images of undoped and Mg doped ZnO films. As seen in Fig. 4(a) shape of ZnO film structure is hexagonal and surface morphology is homogeneous and compact. In Fig. 4(b) doped Mg structures can be seen. Similarly morphology of surface is homogenous too.

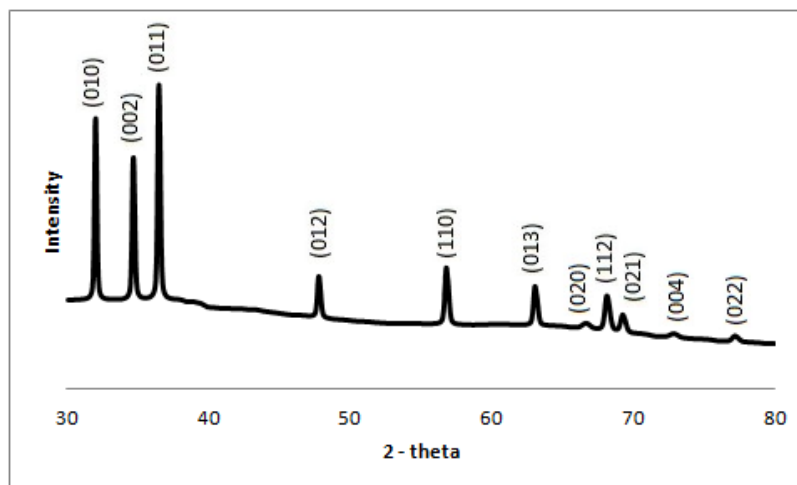


Figure 1. XRD pattern of undoped ZnO film

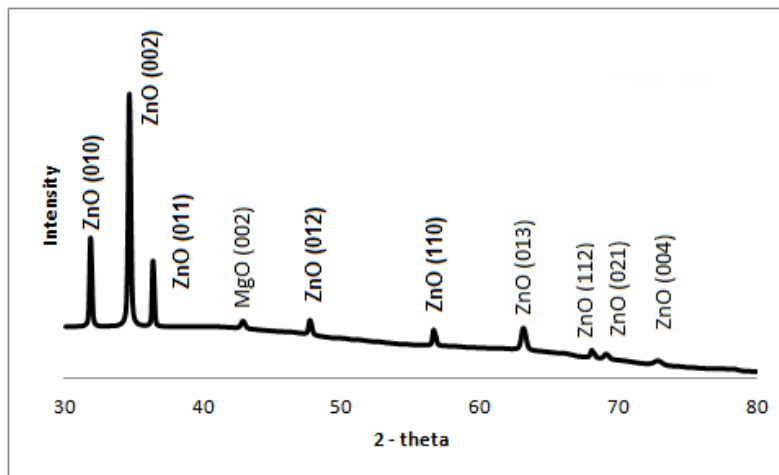


Figure 2. XRD pattern of Mg doped ZnO film

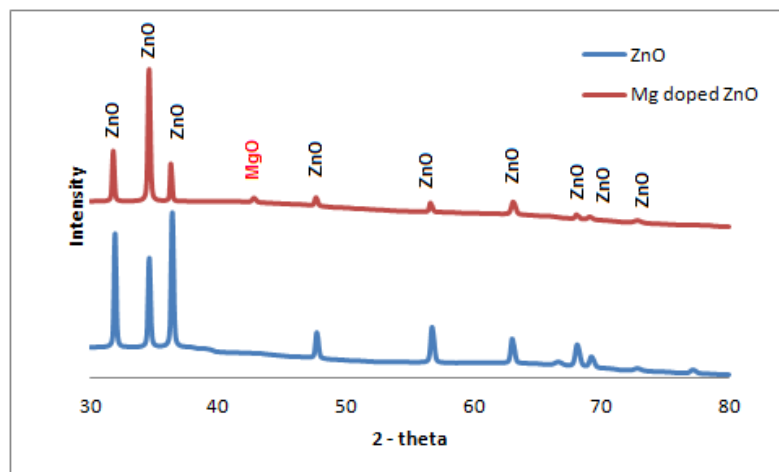


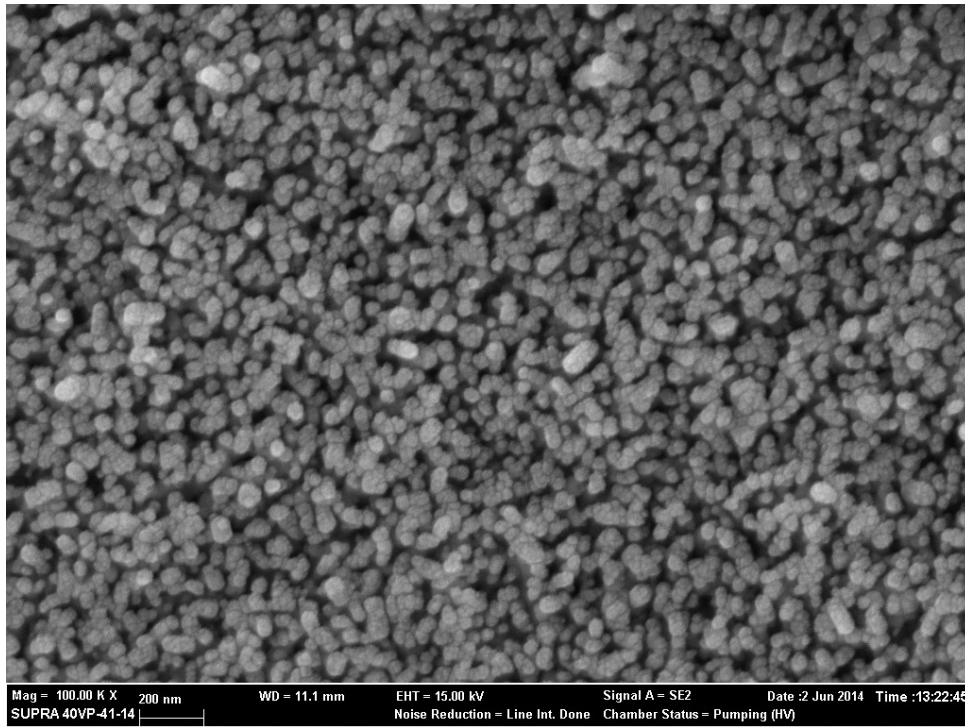
Figure 3. XRD pattern of undoped and Mg doped ZnO films

3.2 Optical properties

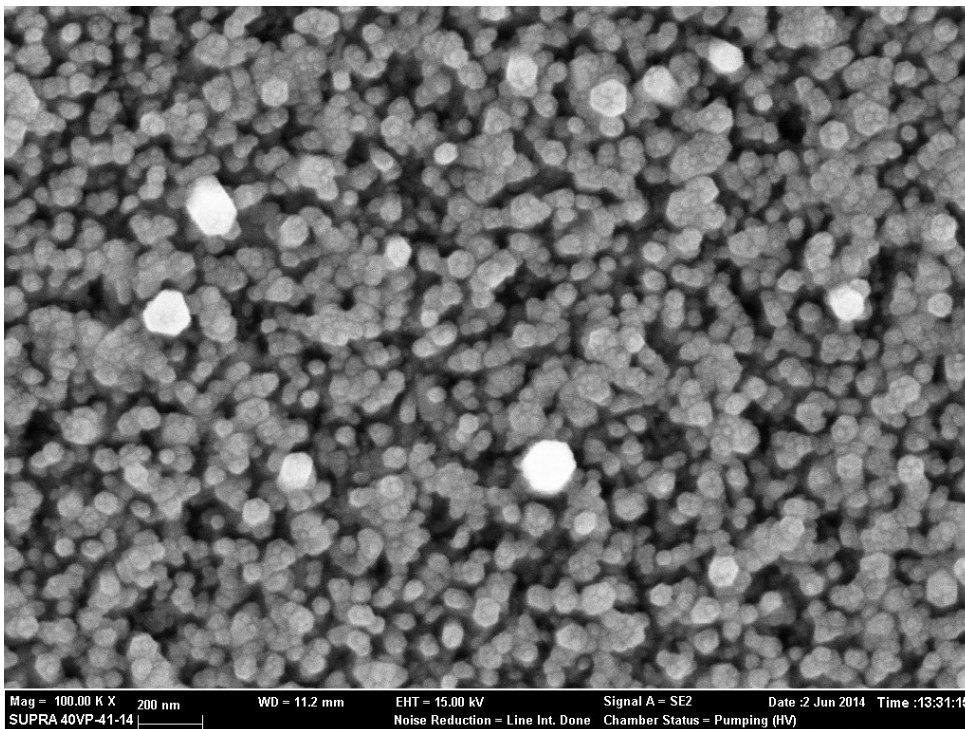
Absorption studies in the UV-Vis. region were carried out at room temperature to determine the optical band gap of the films. UV-Vis spectroscopy measurements were analysed by Perkin Elmer Lambda 25 UV-Vis Spectrometer between 300-1100 nm wavelengths. In Fig. 5 absorption spectra of undoped and Mg doped ZnO films can be seen. The fundamental absorption edge of the films corresponds to electron transitions from valance band to conduction band and this edge can be used to calculate the optical band gap of the films. Undoped and Mg doped ZnO films have a direct transition band gap. In the direct transition, the absorption coefficient can be expressed by (Pankove 1971):

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (1)$$

Where A is a constant, $h\nu$ is the foton energy and E_g is the optical band gap. Fig. 6 shows plots of $(\alpha h\nu)^2$ vs. $h\nu$. The E_g values of the films were calculated from theses plots and are given in Table 1. As seen from these plots, E_g values of films increased with Mg doping.



(a)



(b)

Figure 4. FESEM images of (a) undoped ZnO (b) Mg doped ZnO films

Table 1. Energy band gap values

Films	E_g (eV)
ZnO	3,32
Mg doped ZnO	3,48

Optical transmittance measurements were analysed by Perkin Elmer Lambda 25 UV-Vis Spectrometer between 300-1100 nm wavelengths. In Fig. 7 optical transmittance spectra of films are shown. Transmittance values of films decreased with Mg doping.

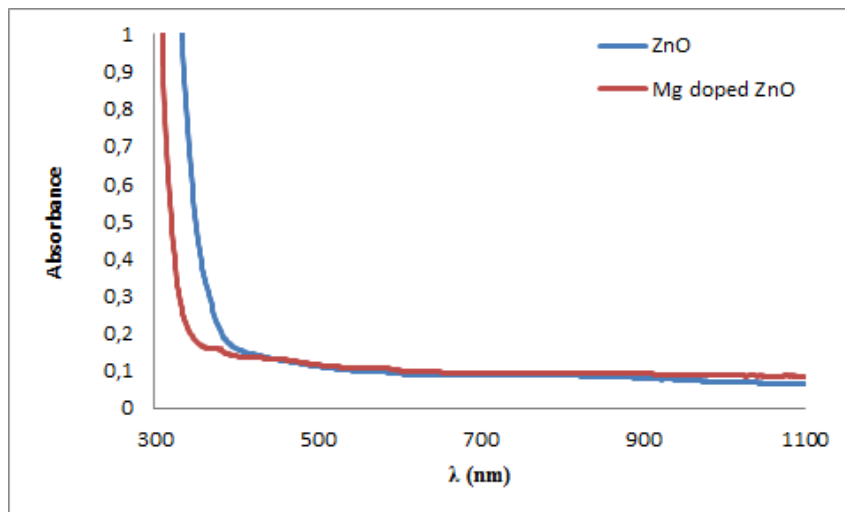


Figure 5. Absorbance spectra of undoped and Mg doped ZnO film

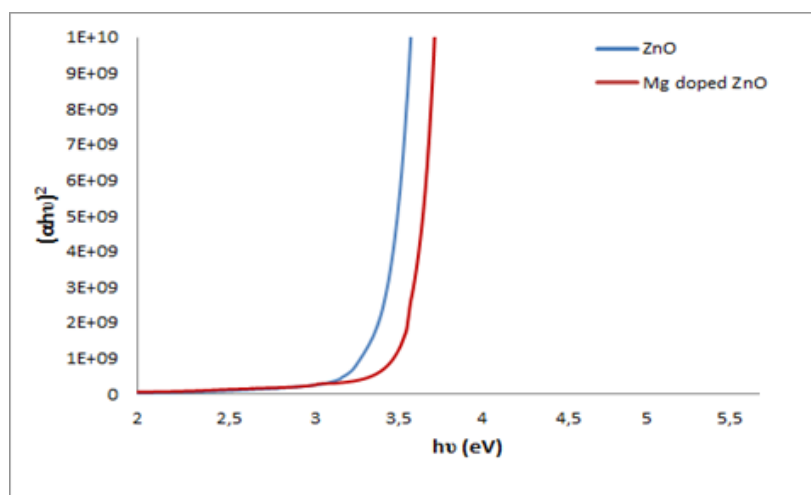


Figure 6. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ of undoped and Mg doped ZnO film

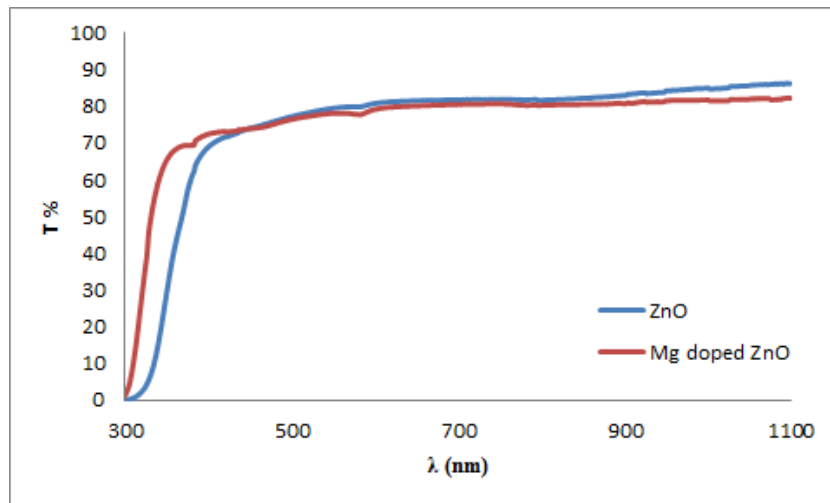


Figure 7. Optical transmittance spectra of undoped and Mg doped ZnO film

4. Conclusion

Undoped and Mg doped ZnO films were deposited on glass substrate by sol-gel spin coating method. Effect of Mg doping on the structural, morphological and optical properties of these films were investigated. The XRD spectra indicate that the films are of polycrystalline nature. In the XRD spectra of Mg doped ZnO films, Mg segregates in the form of MgO (002). The FESEM images clearly depict the homogenous and compact nature of the samples. Furthermore, doped Mg structures can be seen. The band gap is successfully tuned from 3.32 to 3.48 eV with Mg doping. This band gap tuning is well acknowledged by the shift of (002) peak in XRD spectra. The shift in the band gap of ZnO by Mg doping, provides several advantages for electro-optical applications in comparison to undoped ZnO films. The films prepared by this method are easy to prepare, low cost and effective so can be a good candidate for many applications.

References

- Bhattacharya, P., R. R. Das and R. S. Katiyar (2004). "Comparative study of Mg doped ZnO and multilayer ZnO/MgO thin films." *Thin Solid Films* 447: 564-567.
- Caglar, M., J. S. Wu, K. Y. Li, Y. Caglar, S. Ilican and D. F. Xue (2010). "Mg_xZn_{1-x}O (x=0-1) films fabricated by sol-gel spin coating." *Materials Research Bulletin* 45(3): 284-287.
- Cho, J. Y., S. W. Shin, Y. Bin Kwon, H. K. Lee, K. U. Sim, H. S. Kim, J. H. Moon and J. H. Kim (2011). "The effect of Mg_{0.1}Zn_{0.9}O layer thickness on optical band gap of ZnO/Mg_{0.1}Zn_{0.9}O nano-scale multilayer thin films prepared by pulsed laser deposition method." *Thin Solid Films* 519(13): 4282-4285.
- Kaushal, A. and D. Kaur (2009). "Effect of Mg content on structural, electrical and optical properties of Zn_{1-x}Mg_xO nanocomposite thin films." *Solar Energy Materials and Solar Cells* 93(2): 193-198.
- Liang, S., H. Sheng, Y. Liu, Z. Huo, Y. Lu and H. Shen (2001). "ZnO Schottky ultraviolet photodetectors." *Journal of Crystal Growth* 225(2-4): 110-113.
- Minemoto, T., T. Negami, S. Nishiwaki, H. Takakura and Y. Hamakawa (2000). "Preparation of Zn_{1-x}Mg_xO films by radio frequency magnetron sputtering." *Thin Solid Films* 372(1-2): 173-176.



Moon, J. Y., H. Kim and H. S. Lee (2013). "Effect of Cu-doping on the microstructural and optical properties of Mg_{0.2}Zn_{0.8}O thin films prepared by sol-gel spin coating." *Thin Solid Films* 546: 461-466.

Ohtomo, A., M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda and Y. Segawa (1998). "Mg_xZn_{1-x}O as a II-VI widegap semiconductor alloy." *Applied Physics Letters* 72(19): 2466-2468.

Pankove, J. I. (1971). *Optical processes in semiconductors*. Englewood Cliffs, N.J., Prentice-Hall.

Saito, N., H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi and K. Koumoto (2002). "Low-temperature fabrication of light-emitting zinc oxide micropatterns using self-assembled monolayers." *Advanced Materials* 14(6): 418-+.

Sharma, A. K., J. Narayan, J. F. Muth, C. W. Teng, C. Jin, A. Kvit, R. M. Kolbas and O. W. Holland (1999). "Optical and structural properties of epitaxial Mg_xZn_{1-x}O alloys." *Applied Physics Letters* 75(21): 3327-3329.

Shimakawa, S., Y. Hashimoto, S. Hayashi, T. Satoh and T. Negami (2008). "Annealing effects on Zn(1-x)Mg(x)O/CIGS interfaces characterized by ultraviolet light excited time-resolved photoluminescence." *Solar Energy Materials and Solar Cells* 92(9): 1086-1090.

Wang, M., E. J. Kim, S. Kim, J. S. Chung, I. K. Yoo, E. W. Shin, S. H. Hahn and C. Park (2008). "Optical and structural properties of sol-gel prepared MgZnO alloy thin films." *Thin Solid Films* 516(6): 1124-1129.

Zhang, X., X. M. Li, T. L. Chen, J. M. Bian and C. Y. Zhang (2005). "Structural and optical properties of Zn_{1-x}Mg_xO thin films deposited by ultrasonic spray pyrolysis." *Thin Solid Films* 492(1-2): 248-252.

Biographies

Derya PEKER is a Lecturer and Researcher in Eskisehir Osmangazi University, Physics Department in TURKEY. She obtained her PhD in Physics in the field of Solid State Physics from Eskisehir Osmangazi University. Her research interests are focused on: semiconductors, thin films and thin film characterization.

Sinan TEMEL is studying for a PhD degree in Physics in the field of Solid State Physics in Eskisehir Osmangazi University, Physics Department in TURKEY. Also, he is a Research Assistant in Bilecik Seyh Edebali University, Central Research Laboratory in TURKEY.

Murat NEBİ is studying for a PhD degree in Physics in the field of Solid State Physics in Eskisehir Osmangazi University, Physics Department in TURKEY.