OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 2, No. 11, November 2008, p. 714 - 718

Influence of post annealing on the structural and optical properties of $Mg_xZn_{1-x}O$ films

B. K. SONAWANE, M. P. BHOLE, D. S. PATIL*
Department of Electronics, North Maharashtra University, Jalgaon, [Maharashtra], India

Structural and optical properties of $Mg_xZn_{1-x}O$ (x = 0.05) films grown on microscopic glass substrates by sol-gel technique were investigated. Zinc acetate dihydrate, Magnesium acetate as starting precursors and ethanol as a solvent were used to prepare the gel solution. These deposited films were annealed at three different temperatures and characterized by X-ray Diffractometer (XRD), Scanning Electron Microscopy (SEM) and UV-VIS Spectrophotometer for studying structural and optical properties. Energy dispersive analysis by X-ray (EDAX) was used to determine incorporation of Mg content into ZnO. EDAX spectra clearly show the incorporation of Mg into the ZnO films. XRD spectrum reveals that the deposited Mg doped ZnO films were polycrystalline in nature. Crystallinity of these films was found to be increase with increase in post annealing temperature. Optical band gap of $Mg_xZn_{1-x}O$ annealed films was found to be increased from 3.33 to 3.37eV as estimated from both transmission spectra and the absorption coefficients. The band gap was observed to be blue shifted with increasing annealing temperature.

(Received September 7, 2008; accepted October 6, 2008)

Keywords: Post annealing, $Mg_xZn_{1-x}O$, Sol gel, Structural properties, SEM, UV-VIS, EDAX, XRD

1. Introduction

Zinc oxide (ZnO) is an inexpensive wide band gap (3.2 eV) semiconductor with high luminous transmittance, good electrical conductivity, excellent substrate adherence and hardness [1]. ZnO and its alloys are having vast device applications such as solar cells, transparent conducting electrode for display panels, light emitters, sensors, varistors, Ultra Violet detectors, modulators and surface acoustic wave devices (SAW) [2-4]. It crystallizes in a hexagonal wurtzite structure with lattice parameters of c = 5.205 Å, a = 3.249 Å [5]. Due to very small difference in the ionic radius of Mg^{2+} (0.57 Å) and Zn^{2+} (0.60Å), relative lattice distortion can be caused if Zn is replaced by Mg although the band gap can change greatly [6]. To fabricate $ZnO/Mg_xZn_{1-x}O$ heterostructure devices, ternary alloy of MgZnO has been synthesized to provide wider band gap for cladding layers [7-10]. Recent work on the fabrication of ZnO based double heterostructure waveguide and the possibility of hybrid MgZnO/AlGaN heterojunction shows the immense potential of ZnO based devices in future [11]. To improve the effectiveness of light emitting devices, double heterostructure is used which confines more number of electrons and holes in the active layer resulting in enhancement of the recombination process [9]. Therefore, heterostructure needs the cladding heterolayers of increased wide band gap along with nearly the same lattice constant of active layer so that the interface dislocations can be minimized.

Various deposition techniques can be used for the deposition of $ZnO/Mg_xZn_{1-x}O$ films such as pulsed laser deposition (PLD) [13,14], molecular beam epitaxy (MBE) [15], electron beam evaporation [16], metal organic chemical vapor deposition [17,18], reactive electron beam evaporation [19], r. f. magnetron sputtering [20] and sol-gel method [21-23] etc. Among these techniques, sol-gel technique is very simple, economical and having control over compositions and it does not require vacuum apparatus [24]. As per our knowledge, no body has reported, the effect of annealing temperatures on the $Mg_xZn_{1-x}O$ films for studying structural and optical properties deposited by sol-gel method on the microscopic glass substrates using Zinc acetate, magnesium acetate as precursors and ethanol as solvent.

In this paper, we report the successful deposition of polycrystalline $Mg_xZn_{1-x}O$ films on the microscopic glass substrates for 0.05 m/L of Mg concentration. Deposited films were annealed at three different temperatures and we found that the energy band gap increases from 3.33 to 3.37 eV. This paper has been organized in four sections. Second section of the paper describes the experimental procedure used to deposit the Mg doped ZnO films. The most significant results have been discussed in third section and the last section concludes the paper.

2. Experimental procedure

Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] and Magnesium acetate [$Mg(CH_3COO)_2$] were used as starting precursors. Ethanol [CH_3CH_2OH] was used as a solvent and lactic acid [$CH_3.CHOH.COOH$] was used as reacting reagent for the preparation of gel solution. The solution was prepared by dissolving 2.195 gm of Zinc acetate, 0.1097 gm of Magnesium acetate in 25 ml of ethanol to obtain the 0.05m/l concentration with few drops of lactic acid. The solution was heated at ~80 ^{0}C and stirred on magnetic hot plate with the reflux apparatus to avoid

evaporation of ethanol and to keep the same quantity of the solution for an hour. Initially, the solution became milky white and then converted into the transparent solution after stirring for an hour. Prepared transparent solution was used for the deposition of the MgZnO films. Before deposition, the glass substrates were thoroughly cleaned by chromic acid and acetone. Three films were deposited on microscopic glass substrate in the humidity of 32% at room temperature using homemade spin coater. The speed of the coater was kept at ~2000 rpm for all the films by which the layers of the same thickness can be obtained per coat. For each deposition layer, the spinning time was kept one minute. The coating procedure was repeated for six times to achieve the desired film thickness. After each coating, the films were pre-annealed at 250 ^{0}C for 10 minutes to evaporate the solvent. Finally, the samples were annealed at 300^{0}C, 400^{0}C and 500^{0}C for an hour to burn organic compounds and crystallize the MgZnO compound. After annealing, it was observed that all the deposited films were 75 % transparent in nature.

The optical properties were studied by Chemico spectra scan UV-2700 double-beam spectrophotometer. Bruker AXS-D8 X-ray diffractometer (XRD) having source of Cu-K_α and wavelength 1.54056Å was used to obtain the structural information of the films. The surface morphology and elemental composition of deposited films were studied by using JEOL Scanning Electron Microscopy (SEM).

3. Results and discussion

The effect of post annealing temperature on the structural and optical properties has been investigated and the most significant results have been discussed in this paper. Fig. 1 shows the recorded optical transmission spectra of $Mg_xZn_{1-x}O$ films deposited on the microscopic glass substrate for the 0.05 mole concentration. The films were highly transparent (~75%) in the visible spectral range of 400-700 nm at room temperature. It was found that the absorption edge shifts towards the lower wavelength with increasing annealing temperature. The optical band gap of the films was determined from transmission spectra. The energy band gap of deposited films goes on increasing almost linearly from 3.33 eV up to 3.37eV for the temperature 300^{0}C to 500^{0}C. This indicates that the band gap can be increased and monitored by post annealing films at different temperature. By doping Mg in ZnO for the 0.05 mole concentration and annealing at the different growth temperature, energy band gap was increased up to 3.37eV for the 500^{0}C on microscopic glass substrates. MgZnO alloy has similar structure as ZnO, therefore MgZnO is suitable material for the cladding layer in ZnO based device and good quality heterojunction could be made. The composition variation in the film is due to the difference of the vapor pressure between Mg and Zn species at high growth temperature [13]. Zn related species have a higher vapor pressure and can be easily absorbed at higher growth temperature yielding Mg enriched films. Furthermore, the transmission spectra do not show two absorption edges, which suggest that scattering detect centers remains unaffected with the variation of Mg content. This result verifies the optical high quality of MgZnO films. The absorption edge shifted to a short wavelength as the ratio of Mg/Zn increased from sample BG01 to sample BG03 due to increase in post annealing temperature. The crystal quality of sample BG03 observed to be enhanced [6] obviously. Therefore, energy band gap of films increases as post annealing temperature increases.

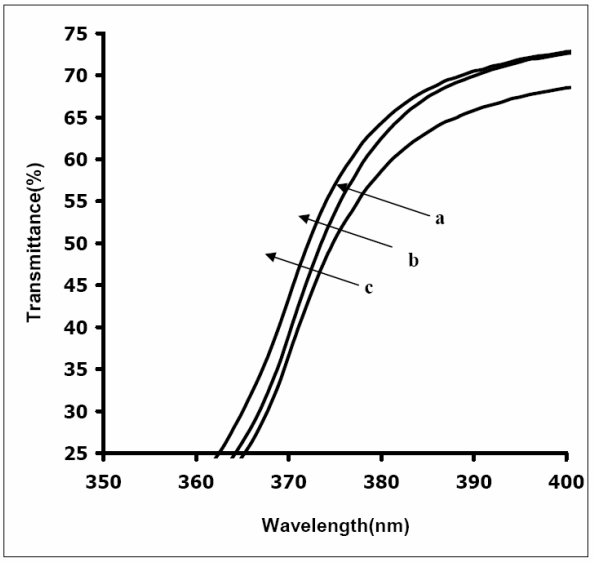

Fig. 1 Optical transmittance spectra of $Mg_xZn_{1-x}O$ films for a) 300^{0}C, b) 400^{0}C, c) 500^{0}C annealing temperatures.

The MgZnO film crystal structure was observed in θ-2θ mode with 0.1 step size. The XRD spectra recorded for deposited films at the different annealing temperatures between the diffraction angle ranges of 20^0 to 60^0 are as shown in Fig. 2. In our result, the XRD peak position of $Mg_xZn_{1-x}O$ films is similar to those reported by D. Zhao et. al [21]. The large hump obtained at 2θ value of 20^0 to 30^0 corresponds to the glass substrate [25] and the three main peaks of (100), (002) and (101) appeared at approximately 31.7, 34.5 and 36.2 attributed to ZnO material. These XRD peaks are associated with the JCPDS card no. 36-1451 of hexagonal ZnO structure. It was observed from the XRD spectra that all present three diffraction peaks were strong and dominant which were attributed to polycrystalline nature of MgZnO films. However, the intensity of diffraction peaks was found to be increasing with increasing annealing temperature and it was greater for 500^{0}C in our results. The full width half maximum (FWHM) of the deposited films was obtained from the peak diffracting at angle 36.2. It was observed that FWHM of the diffraction peaks decreases as annealing temperature increases. It indicates that by increasing annealing temperature, crystal quality of the deposited films gets enhanced.

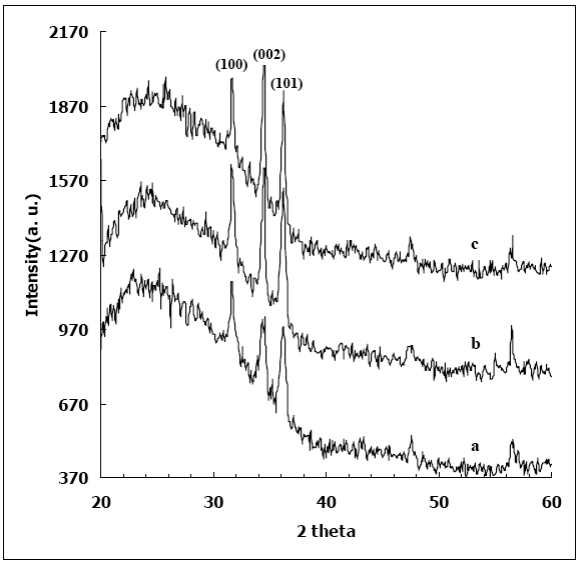

Fig. 2. XRD spectra of $Mg_xZn_{1-x}O$ thin films at different annealing temperatures.

The size of the grains of the MgZnO films was obtained by substituting values of FWHM in the well-known Scherrer's formula [22],

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

where D is mean grain size of crystallite, λ (= 1.54059 Å) the wavelength of the X-ray source used, β the broadening of diffraction line measured at half of it's maximum intensity in radians (FWHM) and θ the angle of diffraction at the peak. The grain size values of the crystalline MgZnO films are 15 nm, 19 nm and 25 nm at the annealing temperatures 300^0C, 400^0C and 500^0C respectively. The detailed data obtained for MgZnO films from the XRD spectra and absorption coefficient has been listed in the Table 1, which gives the detail information about grain size, FWHM and energy band gap for corresponding samples with respect to post annealing temperature. The thickness of the MgZnO films was measured by using well-known Tolansky method.

Table 1. Data obtained from XRD and transmission/absorption spectra.

Sample No.	Annealing Temp.(^{0}C)	FWHM (degree)	Thickness (nm)	Grain size(nm)	Energy Bandgap(eV)
BG01	300	0.58	196	15	3.33
BG02	400	0.45	225	19	3.35
BG03	500	0.34	239	25	3.37

Fig. 3 shows the variation in FWHM of the films in accordance with the annealing temperature. The FWHM of the diffraction peaks goes on decreasing as post annealing temperature increases. This indicates that the crystallinity of the film depends on the post annealing temperature. Fig. 4 illustrates the grain size of the MgZnO particles goes on increasing as annealing temperature increases. Therefore, from above observations of FWHM and grain size, it clearly reveals that the crystal quality of film depends on post *annealing* temperature.

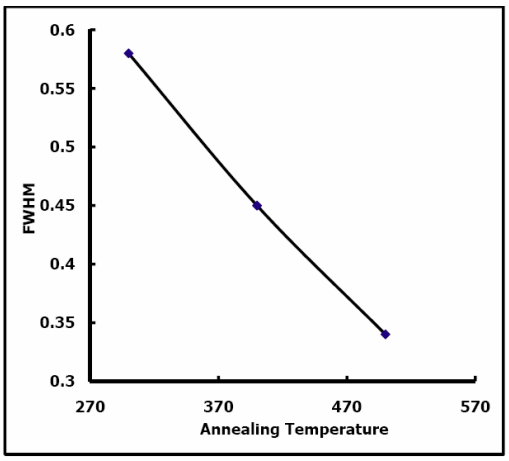

Fig. 3. Variation of FWHM of $Mg_xZn_{1-x}O$ films.

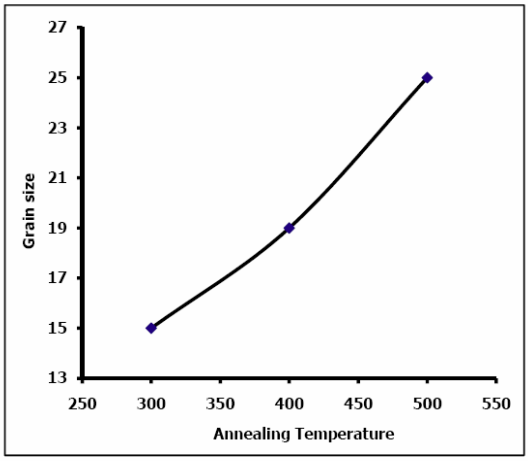

Fig. 4. Grain size of $Mg_xZn_{1-x}O$ films(x= 5 %) obtained from FWHM.

Fig. 5 depicts the variation of squared absorption coefficient (α^2) as a function of photon energy of MgZnO films. Energy band gap was determined from the absorption coefficient and photon energy. The absorption coefficient was calculated from the following formula [6],

$$\alpha^2 = (A/h\nu)^2(h\nu - E_g)$$

where, α is absorption coefficient, A is a constant and hν is a photon energy. The band gap (E_g) can be obtained by plotting (α^2) verses hν and the linear extrapolation to α = 0 and it was found to be increase from 3.33 to 3.37 eV with post annealing temperature. The shift of the optical band gap towards higher value suggests that crystallinity of the films go on increasing. The energy band gap determined from optical transmission spectra and absorption coefficient are nearly matching. It is clear from the above results that hexagonal wide band gap Mg doped ZnO films were deposited.

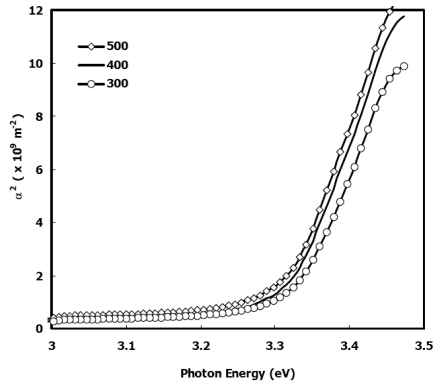

Fig. 5 Variation of absorption coefficient (α) with annealing temperature.

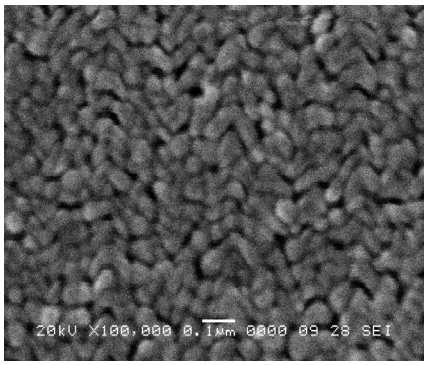

Fig. 6. SEM image for the $Mg_xZn_{1-x}O$ film annealed at 500^0C.

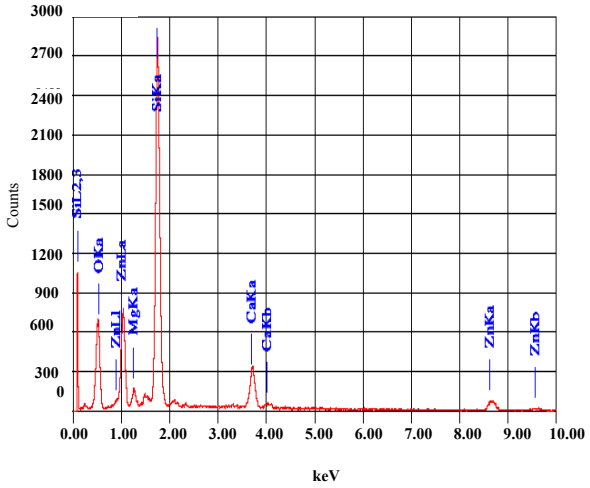

Fig. 7. EDAX spectrum of $MgxZn1_{-x}O$ film annealed at 500^0C.

Fig. 6 and 7 shows the SEM and EDAX spectra of the deposited MgZnO film on microscopic glass substrate for the BG03 sample. SEM picture clearly reveals crystals formed within MgZnO film. The EDAX spectra recorded for the above film shows that the Mg has been incorporated in ZnO successfully using sol-gel technique. The actual mole concentration for the deposition of the films was taken 5 at%. However, the atomic% of Mg incorporated in ZnO of the deposited film as obtained from EDAX was 3 at%. The discrepancy in mole composition was due to incorporation of Mg at interstitial lattice sites and grain boundaries. The other peaks appeared in the EDAX spectra attributed to the impurities added from the glass substrate. The detailed data achieved from the EDAX spectra has given in Table 2.

Table 2. Energy dispersive analysis by X-ray(EDAX) data.

Element	Energy (keV)	Mole Concentration (at%)
O	0.525	63
Mg	1.253	3
Si	1.739	29
Ca	3.690	3.4
Zn	8.630	2.4

4. Conclusions

In this work, MgZnO films were successfully deposited on the soda lime microscopic glass substrates using sol-gel spin coating method. The nature of the films was found to be polycrystalline. The XRD study shows that the crystalline nature was improved by increasing post-annealing temperature. The grain size of MgZnO was found to be dependent on the post annealing temperature. The incorporation of Mg in ZnO was confirmed through EDAX spectrum. Optical band gap was estimated and found to be varying from the 3.33 to 3.37eV with post annealing temperature. In conclusion, we have investigated the effect of post annealing temperature on the polycrystalline MgZnO films.

References

[1] M. H. Aslan, A. Y. Oral, E. Mensur, A. Gul, E. Basran, Sol. Energ. Mat. Sol. C., **82**(4), 543 (2004).
[2] X. Dong, H. C.Zhu, B.L Zhang, X. P. Li, G. T. Du, Semicond. Sci. Techno. **22**, 1111 (2007).
[3] P. Bhattacharya, P. K. Basu, N. Mukharjee, A. Mondal, H. Saha, S. Basu, J. Mater. Sci. Mat. Electron **18**, 823 (2007).
[4] X. B. Wang, J. J. Chan, D. M. Li, key Engineering Materials, **242**, 336 (2007).
[5] Y. S. Cheng, C. T. Chien, C. W. Chen, T. Y. Chu, H. H. Chiang, C. H. Ku, J. J. Wu, C. S. Lin, L. C. Chen, K. H. Chen, J. Appl. Phys. **101**, 033502 (2007).

[6] D. Y. Jiang, D. Z. Shen, K. W. Liu, C. X. Shan, Y. M. Zhao, T. Yang, B. Yao, Y.M. Lu, J. Y. Zhang, Semicond. Sci. Technol. **23**, 035002 (2008).
[7] M. P. Bhole, E.P.Samuel, D. S. Patil,. J. of Modern Optics, **55**(9),1427 (2008).
[8] M. P. Bhole, E.P.Samuel, D. S. Patil, International J. of Modern Physics B, **22**(12), 1985(2008).
[9] E. P. Samuel, M P Bhole, D. S. Patil, Semiconductor Science and Technology, **21**, 993997 (2006).
[10] N. B. Chen, H. Z. Wu, D. J. Qiu, T. N. Xu, J. Chen, W. Z. Shen, J. of phys: Condens. Matter, **16**, 2973 (2004).
[11] R. D. Vispute, V. Talyansky, S. Choopenm R. P. Sharma, T. Venkatesan, M. He, X. Tang, J. B. Halpern, M. G. Spencer, Y. X. Li, L. G. Salamancariba, A. A. Iliadis, and K. A. Jones, Appl. Phys. Lett. **73**, 348 (1998).
[12] H. C. Casey, M. B. Panish, Heterostructure Lasers Part A Fundamental Principals, Academic Press. Inc. Chapter 1, 13.
[13] S. Choopun, R. D. Vispute, W. Yang, R. P. Sharma, T. Venkatesan, H. Shen, Appl. Phys. Lett. **80**(9), 1529 (2002).
[14] A. K. Sharma, J. Narayan, J. F. Muth, C. W. Teng, C. Jin, A. Kvit, R. M. Kolbas, O. W. Holland, Appl. Phys. Lett. **75**(21), 3327 (1999).
[15] H. Tanaka, S. Fujita, S. Fujita, Appl. Phys. Lett. **86**, 192911 (2005).
[16] Y. S. Cheng, C. T. Chien, C. W. Chen, T. Y. Chu, H. H. Chiang, C. H. Ku, J. J. Wu, C. S. Lin, L. C. Chen, K. H. Chen, J. Appl. Phys. **101**, 033502 (2007).
[17] Yu-Sheng Chang, Chih-Tao Chien, Chun-Wei Chen, Ta-Ya. Chu, H. H. Chiang, C. H. Ku, J. J. Wu, C. S. Lin, L. C. Chen, K. H. Chen, J. Appl. Phys. **101**, 033502 (2007).
[18] Xin Dong, Baolin Zhang, Xiangping Li, Wang Zhao, Rensheng Shen, Yuantao Zhang, Xiaochuan Xia, Guotong Du, Semicond. Sci. Technol., **23**, 045020 (2008).
[19] J. Chen, W. Z. Shen, N. B. Chen, D. J. Qiu, H. Z. Wu, J. Phys.: Condens. Matter. **15**, 475 (2003).
[20] D. Y. Jiang, J. Y. Zhang, K. W. Liu, Y.M. Zhau, C. X. Cong, Y. M. Lu, B. Yao, Z. Z. Zhang, D. Z. Shen, Semicond. Sci. Technol., **22**, 687 (2007)
[21] Dongxu Zhao, Yichun Liu, Dezhen Shen, Youming Lu, Jiying Zhang and Xiwu Fan, J. Appl. Phys. **90**(11), 5561 (2001).
[22] M. P. Bhole, D. S. Patil, Opto. Ele. Adv. Mater. (RC), **1**(12), 672 (2007).
[23] M. P. Bhole, D. S. Patil, Modern Physics Letters B, **22**(9), 685 (2008).
[24] M. S. Bhuiyan, M. Paranthan, K. Salama, Supercond. Sci. and Technol (Review), **19,** R_1 (2006).
[25] F. Yakuphanoglu, S. Ilican, M. Caglar, J. Optelectron. and Adv. Mater., **9**(7), 2180 (2007).

*Corresponding author: patildsp@rediffmail.com