ASM Sc. J., 13, 2020
https://doi.org/10.32802/asmscj.2020.sm26(2.20)

Structural and Optical Properties of ZnO and MgZnO Semiconductor Materials at Different Annealing Temperature

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Zinc Oxide (ZnO) and Magnesium Zinc Oxide (MgZnO) had received much attention in photoelectronic devices. The current study is performed to investigate the effect of temperature on the structural and optical properties of ZnO and MgZnO with 99.99% purity, deposited on Indium Tin Oxide (ITO) glass using Radio Frequency (RF) magnetron sputtering technique. The Argon flow into the chamber is 10 sccm with a deposition rate of 0.25± 0.1 kA/s, working pressure 4.5 x 10-3 Torr, gas and RF power of 100 watt. Structural analysis using X-Ray Diffraction (XRD) shows that when the temperature increase, the diffraction peak intensity and grain size increase while the deposition time at 30 minutes shows the best intensity. The grain size of ZnO and MgZnO is 0.362 nm and 0.195 nm at 3000 C respectively. This shows that the full width half maximum (FWHM) of ZnO is smaller compared to MgZnO. The optical transparency value from UV-Vis spectrophotometer is 78% for ZnO while MgZnO showing 80%. This shows that optical transmittance of MgZnO is slightly higher than ZnO.

Keywords: zinc oxide; magnesium zinc oxide; optical properties; structural properties; radio frequency sputtering.

I. INTRODUCTION

Zinc oxide is a well-known and widely used material. Research of its semiconducting properties was started in 1930, but interest in this material dropped soon because of difficulties to make p-type ZnO layers (Neuman *et. al., 2011*). Undoped ZnO has electron-conducting properties because of naturally occurring oxygen vacancies. The zinc atom adjacent to the vacancy has a free bond and acts like a donor. Interest in ZnO has recently risen again because of the improvement in growth techniques (Neuman et. al., 2011). Those improvements have made the production of UV-emitting MgZnO layers possible (Sukauskas, 2011). Since the ionic radius of Mg^{2+} (0.57 Å) is close to that of Zn^{2+} (0.6 Å) (Pandey & Mukherjee, 2011), the replacement of Zn by Mg should not cause a significant change of the lattice constant. However, a large crystal structure difference between the wurtzite-hexagonal ZnO (a = 3.25 Å and c = 5.21 Å) and the rocksalt-cubic MgO (a = 4.21 Å) can cause unstable phase mixing (Pandey & Mukherjee, 2016; Chen & Kang, 2008). Depending on growth

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conditions, MgZnO may have a cubic or a hexagonal lattice. It is crucial to identify growth conditions which lead to a specific lattice of MgZnO layer (Pandey & Mukherjee, 2011).

The discovery of $Mg_xZn_{1-x}O$ based materials enables one to fabricate ZnO based nano layers and superlattices which are crucial in the fabrication of ZnO based optoelectronic devices (Gruber et al. 2004). To this day, there are a vast numbers of deposition techniques that have been utilized in the preparation of ZnO and MgZnO thin films, among them are radio frequency magnetron (RF) sputtering, pulse laser deposition (PLD) technique, chemical vapour deposition (CVD), and molecular beam epitaxy (Stringfellow, 1999: Remashan *et. al.,* 2010).

Despite the diverse method of deposition technique, based on past research records, a significant amount of research focus on the deposition technique using the RF magnetron sputtering. This is due to the fact that the sputtering method produces a high-quality and homogeneous surface of thin film that has a good adhesive strength (Sukauskas, 2011; Ozgur *et. al.,* 2005). In this paper, ZnO and MgZnO films were both deposited on ITO substrates using the RF magnetron sputtering with varying temperature. The effects of, substrate temperature as well as post-annealing on the properties of MgZnO and ZnO films were then analysed and compared.

II. MATERIALS AND RESEARCH METHOD

ZnO/MgZnO thin films were deposited separately on an indium tin oxide (ITO) coated substrates using RF magnetron sputtering. The targets utilized in this research are ZnO and MgZnO with a 99.99% purity with a dimension of 3” in diameter and a 0.125” thickness. The substrates were placed in the ultrasonic bath and were immersed for 10 minutes in distilled water. The process was then repeated with ethanol and acetone. Once cleaned, the substrate was then rinsed again with distilled water and were then blown dried using nitrogen gas.

The deposition of the ZnO and MgZnO thin films using RF sputtering was carried out at room temperature at 9 mili-torr of pressure for 30 minutes. The sputtering power was adjusted to 100 W and substrate rotation was set to 5 rotation per minute, while the argon gas flow was kept at 10 sccm to ensure the homogeneity of the thin film surface.

Once fabrication was completed, the thin films were then placed in a furnace for 30 minutes for heat treatment. The annealing temperature was adjusted to (100^{o}C – 300^o C). The temperature was adjusted accordingly in order to investigate the effect of annealing at various temperature on the properties of both ZnO and MgZnO. The structural and crystalline properties of the individual films were characterized using X-Ray Diffraction (XRD). On the optical properties, samples were analysed by using UV-Vis Spectrometer Lambda EZ210 in the wavelength range from 190 nm to 1100 nm.

III. RESULTS AND DISCUSSION

A. Structural Properties

Based on Table 1, XRD Analysis on the structural properties of both ZnO and MgZnO samples shows that ZnO has greater superiority at all three different annealing temperature. It is observed, that at the highest annealing temperature of 300^{o}C has a smaller value of full width half maximum (FWHM) of 0.46148^o with a grain size of 0.362 nm, while MgZnO sample shows a full width half maximum of 0.85615^o with a grain size of 0.195 nm and an intensity The FWHM is obtained using Scherrer equation as shown in equation (1);

$$d = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

d= Average grain size
λ = the average wavelength of X-rays
β = FWHM
θ = Bragg angle

Based on a research conducted by Neuman *et. al.,* 2011, (Neuman *et. al.,* 2011) it is shown that the effects of MgZnO towards higher annealing temperature improves its crystallinity with greater grain size which agrees to the result obtained from this research. Similarly, the crystallinity of ZnO improves with greater annealing temperature. However, from the FWHM data obtained, it can be justified that, MgZnO is able to withstand greater annealing temperature which agrees to the research conducted by Hwang et al. 2015 where it was detailed that at 900°C of annealing temperature, MgZnO exhibits greater rectification ratio compared to 800°C and is capable of annealing beyond that of ZnO (Chen & Kang, 2008). Based on the XRD result from Figure 1 and Figure 2, ZnO shows better crystallinity with a crystalline phase while MgZnO shows similar broad wave crystalline. Moreover, both MgZnO and ZnO shows improvement on its crystallinity with greater temperature. Further analysis with the calculation of crystallite grain size of ZnO and MgZnO shows the variations of full width half maximum (FWHM) and its relation to the crystallite grain size as the functions of temperature as shown in Figure 3 and Figure 4.

Table 1. The Full Width Maximum (FWHM), intensity and grain size of ZnO and MgZnO at different annealing temperature

Sample	Annealing temperature (°C)	FWHM (°)	Intensity (a.u)	Grain size (nm)
ZnO -(1	100	0.48455	223.9	0.345
ZnO -(2)	200	0.47769	243.9	0.350
ZnO -(3)	300	0.46148	308.4	0.362
MgZnO -(1)	100	0.94005	80.15	0.177
MgZnO -(2)	200	0.87686	84.83	0.190
MgZnO -(3)	300	0.85615	91.75	0.195

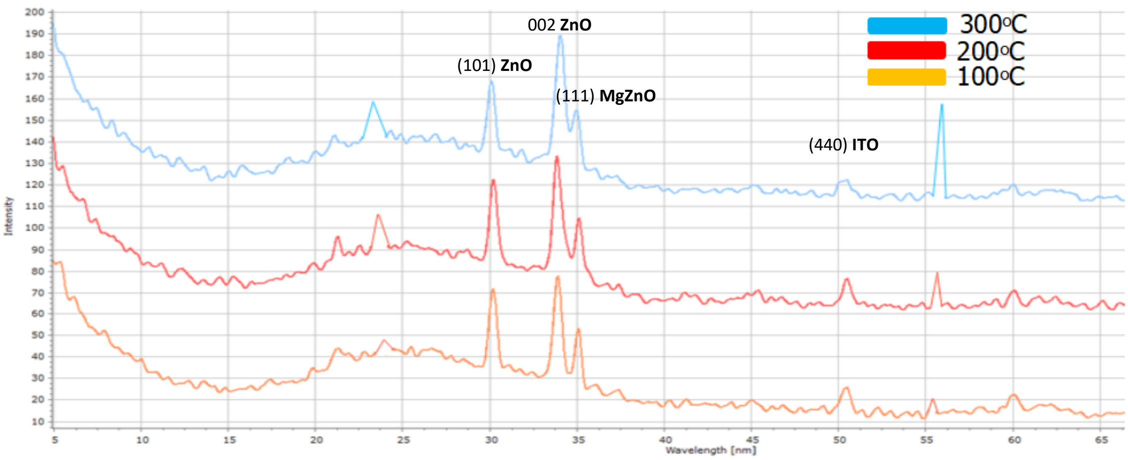


Figure 1. XRD pattern of MgZnO thin films with variant substrate temperature

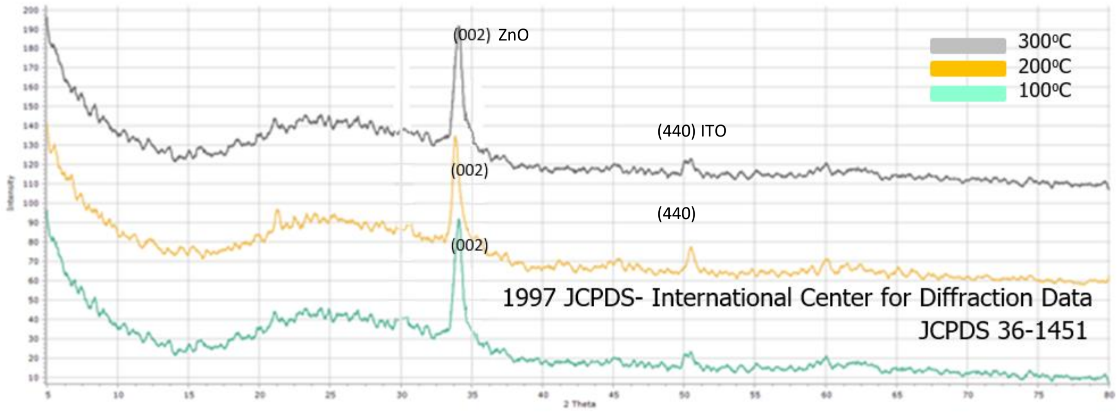


Figure 2. XRD pattern of ZnO thin films with variant substrate temperature

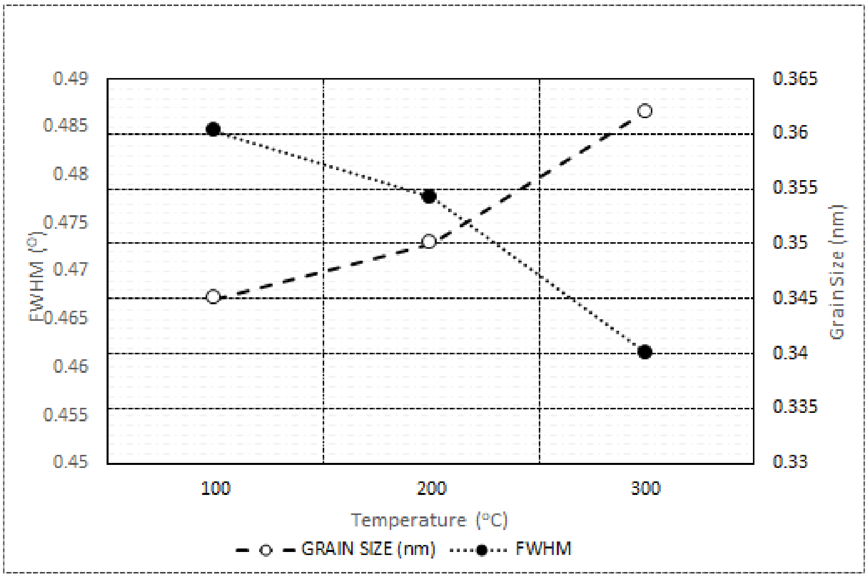


Figure 3. Variations of Full Width Half Maximum (FWHM) and Crystallite Grain Size as the functions of substrate temperature of ZnO

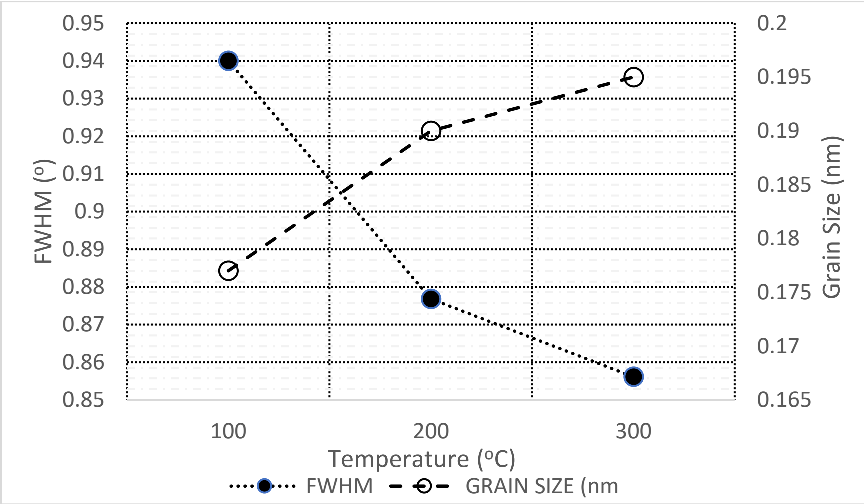


Figure 4. Variations of Full Width Half Maximum (FWHM) and Crystallite Grain Size as the functions of substrate temperature of MgZnO

B. *Optical Properties*

Based on the analysis obtained from the UV-Vis spectrometer, as the annealing temperature is increased the optical transparency becomes clearer. The transmittance of ZnO was only about 50% while MgZnO shows greater transparency of 80% at 300°C. This result is due to the shift in the absorption edge in the lower wavelength region as compared to the ZnO thin film based on the transmittance vs wavelength graphed in Figure 5. From the optical transmittance, the direct band gap of ZnO and MgZnO thin films can be calculated using the intercept of $(\alpha h\upsilon)^2$ vs photon energy ($h\upsilon$) plot. Utilizing Beer's Law equation.

$$I = I_O e^{-\alpha d} \quad (2)$$

$$\alpha = \frac{ln(\frac{1}{T})}{d} \quad (3)$$

$$(\alpha h v)^{1/n} = A(hv - E_g) \quad (4)$$

I_o = Initial intensity of light beam entering a sample

I = Intensity of emitted radiation

α = Optical Transmittance

d = Thickness of film

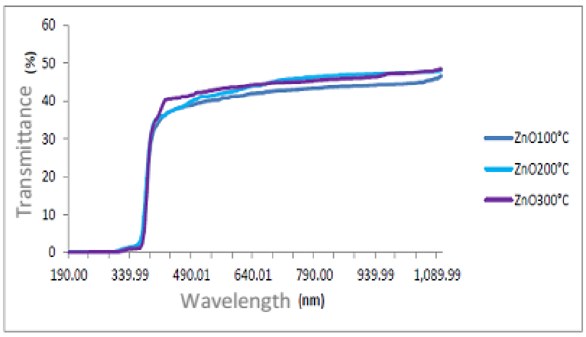
T= Transmittance

h = Planck's constant

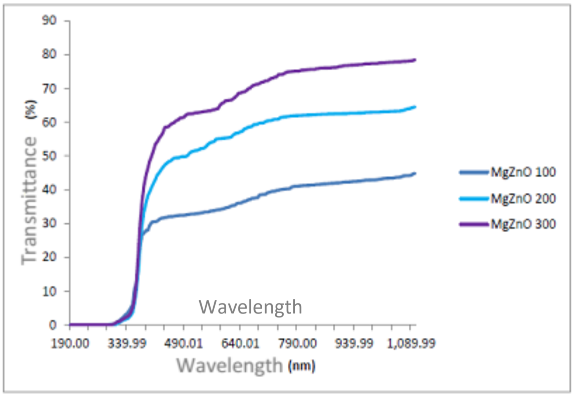
υ = wavelength

E_g = Band gap

Based on the calculated data, as the annealing temperature is increased, the optical band gap is increased as well. For ZnO, the band gap observed for 100°C, 200°C and 300°C are 3.5eV, 3.55 eV and 3.65 eV. Based on several research (Sukauskas, 2011; Stringfellow, 1999) the optimum band gap for Zinc Oxide ranges from 3.3eV to 3.4eV. The changes in band gap is due to the increment of the separation between the valence and conduction band (Liu et al. 2009). However, the band gap for ZnO still retains its semiconductor properties as it does not exceed 4.5eV. While for MgZnO, the optical band gap at 100°C, 200°C, 300°C are 3.58eV, 3.65eV and 3.72eV. The increment of the band gap value agrees to the previous research conducted (Neuman *et. al.,* 2011).

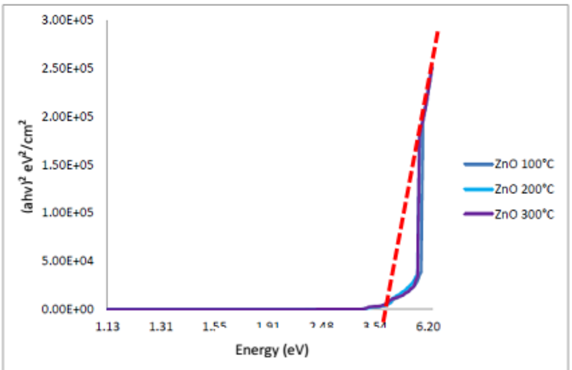


(a)

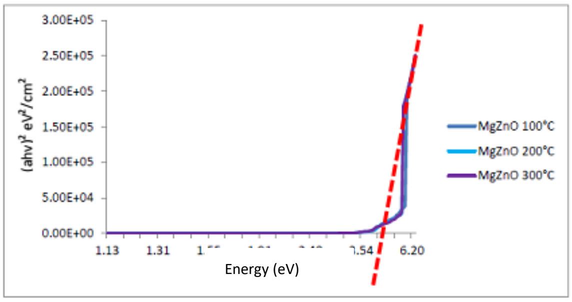


(b)

Figure 5. Optical Transmittance of (a) ZnO and (b) MgZnO



(a)



(b)

Figure 6. Optical Band gap of (a) ZnO and (b) MgZnO

IV. SUMMARY

In this paper, the effects of annealing temperature on ZnO and MgZnO had been investigated. The structural properties of ZnO shows that it has better crystallinity with a grain size of 0.362 nm in comparison to MgZnO with a grain size of 0.195nm as observed at the highest annealing temperature. This indicates that ZnO has a greater ratio of grain boundary to dislocations. In terms of optical transmittance, MgZnO is a more suitable candidate for the implementation of invisible circuitry where it has an optical transmittance over 80%.

V. ACKNOWLEDGEMENT

This research was supported by the Ministry of Higher Education Fundamental Research Grant Scheme (FRGS) 2016 under the project code of FRG0448-STG-1/2016 and University Malaysia Sabah with the project code GUG0131-1/2017 and SDK0075-2019. The support from both parties are greatly acknowledged and appreciated.

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