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ORIGINAL ARTICLE

Piezoelectric Properties of Mg Doped ZnO Thin Film using Sol-Gel Method and Spin Coating

N.S. Ab Sukor[1], A.G.E. Sutjipto[*], A. Shaitir and M.A. Jusoh[1]

[1]Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebihraya Tun Razak, 26300 Gambang, Pahang, Malaysia.

ABSTRACT – This reports about the synthesis of Mg doped ZnO thin film using spin-coating techniques through sol-gel method. For studying piezoelectric properties, optical properties and morphology, the prepared Mg doped ZnO thin film samples were characterized using Ultraviolet-Visible Spectroscopy (UV-Vis), Photoluminescence Spectroscopy (PL), X-ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and Ultrasonic Vibrator. The particle size was evaluated using Scherrer's formula from XRD patterns. The results show the crystallite size decreased with increasing Mg concentrations. The optical properties showed that sample exhibit a blue shift in absorption in UV spectra indicating good optical properties. The morphology of grain size microstructure was observed from FESEM with results the grain size of the samples decreased with increasing Mg doping. The piezoelectric properties were evaluated using ultrasonic vibrator and multimeter to obtain potential difference for each sample. The results obtained that potential difference increase with increasing Mg contents and higher rotation of spin speed was used.

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INTRODUCTION

Zinc oxide (ZnO) is a versatile material containing a vast range of properties, including good transparency, high thermal conductivity, room-temperature solid luminescence, high electron mobility, and wide band gap. It can be used in many application devices such as laser diodes, solar cell, gas sensors, light-emitting diodes (LED), surface acoustic waves, thin-film transistors (TFT), and field emission devices [1]. The transparent oxide semiconductor is suitable in transparent and flexible electronics. The ZnO has excellent semiconducting properties, which has a direct wide band gap of 3.37 eV lying near UV range and large excitation binding energy of 60 meV at room temperature for optoelectronics device fabrication. Metal-doped ZnO and ZnO have good optical and electrical properties as ZnO doped with a metal such as magnesium improves oxide semiconductors' electrical performance [2].

There are various techniques (vacuum and non-vacuum) to synthesis ZnO thin film, such as chemical vapour deposition (CVD), sputtering, molecular beam epitaxy (MBE), sol-gel process, pulse laser deposition (PLD), and spray pyrolysis. On the other hand, the sol-gel method using spin coating techniques is used because of its ease to dope, simplicity, flexibility, acceptable cost and offers to prepare large-area coating but might give the low crystalline quality of ZnO thin film. However, some significant challenges using this process, such as difficulties in preparing a stable dispersion, poor conductivity of ZnO thin films, and uniformity in the coating process [3]. The objectives of this work are to synthesis Mg doped ZnO thin film using the sol-gel method and to fabricate thin film of Mg doped ZnO using spin coater, and to characterize the piezoelectricity of the thin film.

METHODOLOGY

Synthesis of Sol-Gel

Zinc acetate dehydrate and magnesium chloride were dissolved using absolute ethanol in a beaker. The mixture of the solution was stirred by using a magnetic stirrer at 60 °C for 1 hour. The colour of the solution was changed from clear to milky. After one hour, a few drops of diethanolamine (DEA) were added to the mixture until the milky solution turns clear using a dropper. Then, the mixture of the solution was left to continue stirred for another 1 hour. After one hour, a homogenous sol-gel was sealed with parafilm and then deposited for 48 hours.

Fabrication of Mg doped ZnO Thin Film

Pure ZnO and Mg doped ZnO thin films were fabricated onto a glass substrate and aluminium foil through spin coating techniques by varying spin speed. In this work, Laurell WS-650MZ-23 Spin Coater was used to fabricate the thin films. The thin films were fabricated with different spin speeds with a spinning time of 60 second. After one layer of coating, the sample were heated at 80 °C on a hot plate. The process was repeated for 50 times to obtain 50 layers of coating. In this study, 10 wt% and 15 wt% Mg doped ZnO were fabricated at 2000 rpm, while the 5 wt% mixture were fabricated with different spin speeds of 2000, 2500 and 3000 rpm. After the spin coating process, the sample were annealed at a temperature of 400 °C for one hour using Thermo Scientific Lindberg Blue M box furnace. Lastly, all samples were

*CORRESPONDING AUTHOR | A.G.E. Sutjipto | ✉ agusgeter@ump.edu.my

characterized by using XRD, FESEM, UV-Vis, PL and Ultrasonic Vibrator to determine the optical, structural, morphological and piezoelectric properties of thin films.

RESULTS AND DISCUSSION

Optical Properties

Optical properties of the sample was obtained using UV-Vis analysis. UV-Vis was carried out to determine the absorption and transmittance spectrum with different Mg loading and spin rate rotation. Absorbance measurement (A) of the sample in the function of wavelength from 200 – 900 nm was measured. The direct bandgap of samples was determined by OriginPro software using the intercept of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) plot. The optical bandgap of undoped and doped ZnO thin films was obtained by calculated using the Tauc relationship (Eq. 1);

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (1)$$

where E_g is energy bandgap, h is Plank's constant in eV (4.1357×10^{-15} eV.s), υ is the velocity of light (3×10^8 m/s) and α is absorption coefficient.

Table 1 shows the optical bandgap of UV emission at different Mg contents and spin rate. The results show that the optical bandgap value increases with increasing Mg doping in ZnO thin films. The results show an increment in bandgap energy as the amount of Mg dopants increased due to reflectance intensity influences. Perhaps the enhancement in the band gap is due to the incorporation of Mg and its higher concentration, which moves optical reflection to lower energy and widening the energy gap. The dopant can contribute in the optical band gap of ZnO to the width of the localized states [4]. The results also show that the bandgap energy of thin films increases with increasing spin speed. The film thickness depends on the spin rate as the spin rate of spin coating increases, the thinner the thickness of the film would be produced due to the fluid of sol-gel spins off rapidly at the substrate surfaces [5]. The rapid evaporation of spin coating would induced the lattice strain in grown crystal and also brought to the kinetically driven metastable state phase making the orientation of molecular suitable for charge transport [6].

Table 1. The optical band gap of UV emission at different Mg contents and spin rate

Concentration of Mg (wt%)	Spin Speed (rpm)	Optical Band gap (eV)
0	2000	3.28
5	2000	3.13
5	2500	3.30
5	3000	3.31
10	2000	3.32
15	2000	3.33

Figure 1 shows the transmittance spectrum of different Mg contents and a spin rate of Mg doped ZnO thin films. The results reveal transmittance value of thin films that produced with 0, 5, 10 and 15 wt% Mg at constant annealing temperature are 91, 40, 78 and 82%, respectively. In this study, the trend of transmission graph plotted of Mg doped ZnO increases indicate that Mg doping in ZnO increased ultra-violet wavelength transmission of ZnO. It shows that the transparency of thin films affected by the concentration of Mg. The transmittance values of 52000, 52500 and 53000 samples are 40, 86 and 96%. Theoretically, the thin film produced will become thinner when spin speed increases during coating and leads to higher transparency. The transmittance value of 86 and 96% for both 52500 and 53000 indicates that both films could be used in solar cells as transparent conducting oxide electrodes, which is similar to the previous study[5].

Photoluminescence Analysis

Photoluminescence spectrum is an effective way to study the electronic structure, optical and photochemical properties of semiconductor materials through which knowledge such as surface oxygen vacancies and defects can be obtained, as well as the efficiency of charge carrier trapping, immigration and transfer. Figure 2 shows PL spectra of Mg doped ZnO thin films with different spin rates and Mg contents. The result shows show that as Mg concentration increases, the intensity of the ultraviolet emission bands increase to the maximum at 5 wt% Mg doped ZnO, and then decrease at 10 wt% Mg doped ZnO and 15 wt% Mg doped ZnO. The intensity decrease due to increasing energy level during doping, thus, reducing the energy bandgap and simultaneously decreasing in recombination rate of electron and hole.

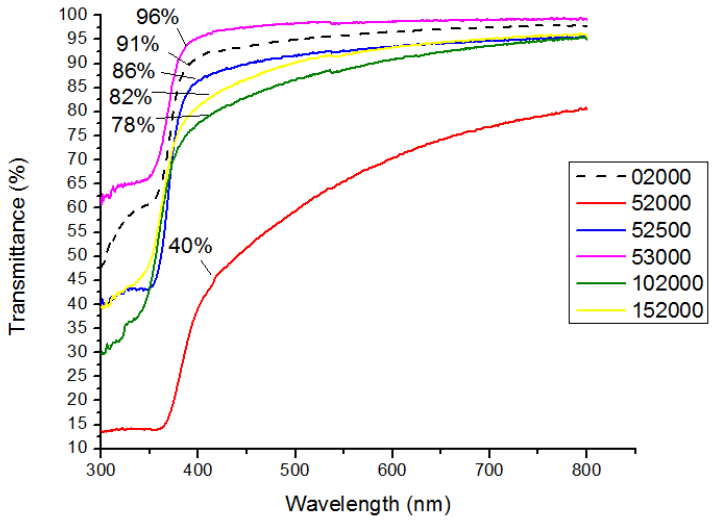

Figure 1. Transmittance spectra of MgZnO thin films by different Mg contents and spin rate

The intensity decrease with a higher Mg concentration as higher doping percent in ZnO prevents recombination of excited electron and hole. Additional active defect sites would produce inside the ZnO lattice when higher doping of Mg content so further adsorption of visible light through active defect sites [2]. The intensity of the ultraviolet emission bands decreased when a higher spin speed was used in the deposition process [7].

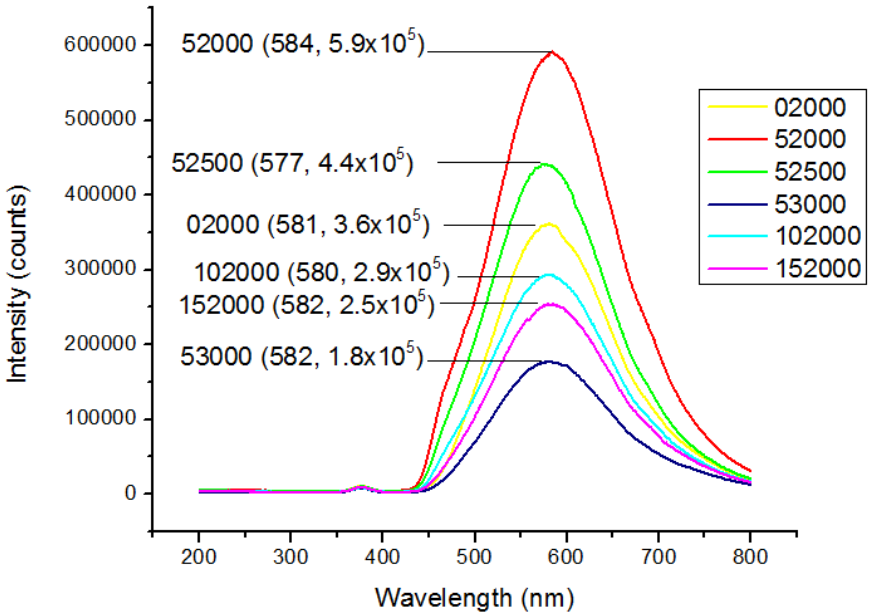

Figure 2. PL spectrum of MgZnO thin films with different spin rate and Mg contents

XRD Analysis

The XRD were used to analyze and determine the composition, phase exists and crystallite size of Mg doped ZnO sample. The crystallite size and d-spacing of Mg doped ZnO thin films were calculated from obtained XRD results. The d-spacing of thin films can be obtained from Bragg's Law which as shown in Eq. 2.

$$d = \lambda/(2\sin\theta) \quad (2)$$

where λ is the wavelength of X-ray (0.15406 nm), d is d-spacing in nm, θ is the Bragg's angle, 2-theta (2θ). The crystallite size was obtained by using Scherrer's formula, as shown in Eq 3.

$$T = 0.9\lambda/(\beta\cos\theta) \quad (3)$$

where T is crystallite size in nanometer, β is full width at half maximum of the peak (FWHM) in radian. In Figure 3, the peak located at ~78°, indicates aluminium peak originated from the substrate. The ZnO phase could be found in the thin

film that oriented in (101) crystal planes at ~38°. Besides, it could be preferentially oriented in (220) crystal plane at ~65°, which corresponds to the MgO phase. Moreover, all samples doped with Mg show the MgO phase formation corresponding to the (220) crystal plane. Figure 3 shows the MgO phase presence, which represents by (220) crystal plane is formed when Mg ions were doped inside the ZnO crystal lattice. However, the ZnO phase is decreased after doping with Mg as the dopant ions may replace Zn ions due to their atomic radii variance and indicate a small amount of strain leads to change the regularity of crystal [2]. Table 2 shows the average crystallite size gradually decreases upon increasing Mg concentration.

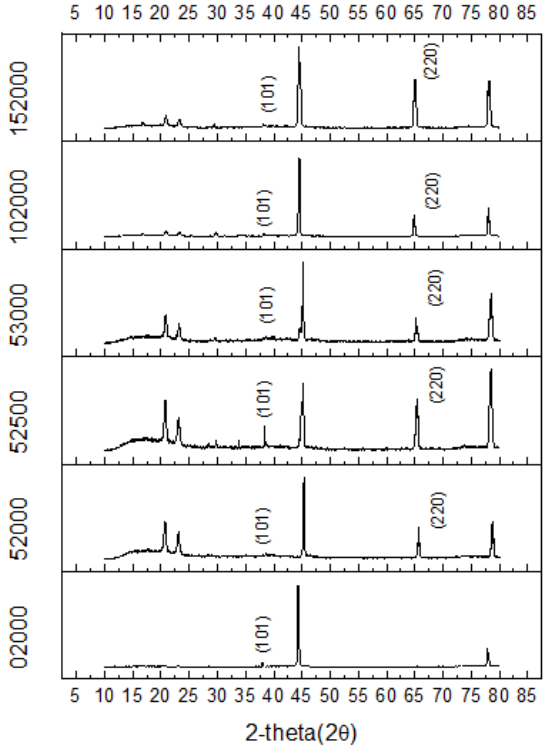

Figure 3. XRD spectrum of each film

Table 2. Crystallite size of diffractions (101) and (220) peaks for MgZnO thin films with different Mg contents and spin rate.

Sample	2-theta (2?)	(h k l)	Crystallite Size (nm)
02000	37.98	(101)	94.46
	-	-	-
52000	38.56	(101)	4.92
	65.68	(220)	63.48
52500	38.34	(101)	46.27
	65.46	(220)	35.99
53000	38.24	(101)	2.45
	65.5	(220)	31.40
102000	38.3	(101)	31.94
	64.94	(220)	54.68
152000	38.14	(101)	28.73
	65.02	(220)	24.50

Morphology Analysis

FESEM was used to analyze and study the surface morphology of pure ZnO and Mg doped ZnO with different Mg concentrations and spin rate at constant heat treatment of 400 °C. Surface morphology of 0 wt% Mg and spin speed of 2000 rpm at a different magnification at several regions of the samples (Figure 4). The result shows the small grains were formed with less porosity in the highest nano-sized measurement around 40 nm to 65 nm. The surface morphology of 5 wt% Mg and spin speed of 2000 rpm shows the surface of samples appears more porosity and cracking structures with inhomogeneous distribution of nanoparticles was formed in highest measurement around 25 nm to 40 nm (Figure 5). Meanwhile, the surface morphology of 5 wt% Mg and spin speed of 2500 rpm shows the surface of samples appears clear circular-shaped nanoparticles, more compact and dense even though they have more porosity than 5 wt% and spin speed

of 2000 rpm (Figure 6). The highest grain size of nanoparticles was around 30 nm to 45 nm. The sample of 5 wt% Mg and spin speed of 3000 rpm show the surface of samples possessed compact clear circular shapes nanoparticles better than 52000 and 525000 and dense distribution of crystalline structure (Figure 7). The highest grain size of the samples was around 20 nm to 60 nm. Furthermore, the sample of 10 wt% Mg and spin speed of 2000 rpm shows the surface of samples consists less porosity, and cracking with a few agglomerations of nanoparticles was observed. The highest grain size of the nanoparticles was around 20 nm to 45 nm (Figure 8). Lastly, the sample of 15 wt% Mg and spin speed of 2000 rpm appears inhomogeneous distribution with more agglomeration of nanoparticles was observed. The highest grain size of nanoparticles was around 20 nm to 60 nm (Figure 9).

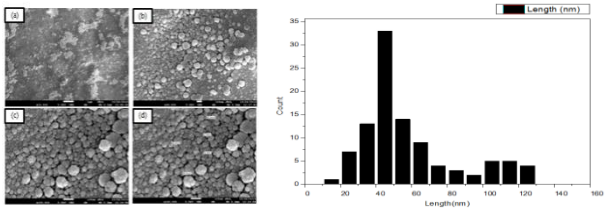

Figure 4. Surface morphology and particles size histogram of ZnO thin films deposited on Al foil with different magnification and spin rate of 2000 rpm (a) 10kx (b) 50kx (c) 100kx

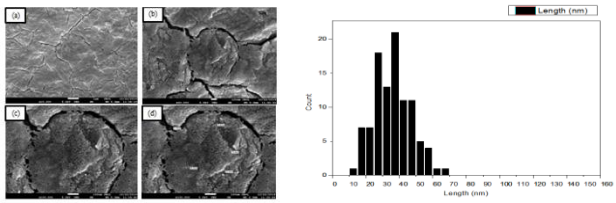

Figure 5. Surface morphology and particles size histogram of 5 wt% Mg doped ZnO thin films deposited on Al foil with different magnification and spin rate of 2000 rpm (a) 10kx (b) 50kx (c) 100kx

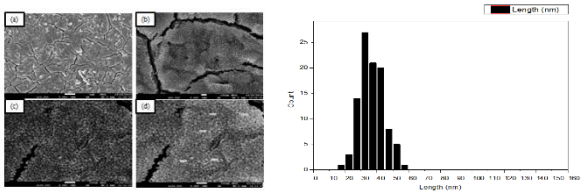

Figure 6. Surface morphology and particles size histogram of 5 wt% Mg doped ZnO thin films deposited on Al foil with different magnification and spin rate of 2500 rpm (a) 10kx (b) 50kx (c) 100kx

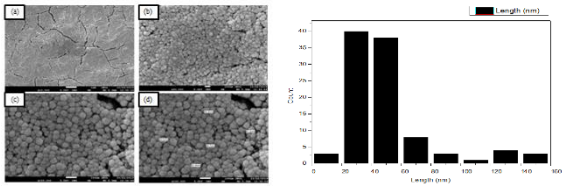

Figure 7. Surface morphology and particles size histogram of 5 wt% Mg doped ZnO thin films deposited on Al foil with different magnification and spin rate of 3000 rpm (a) 10kx (b) 50kx (c) 100kx

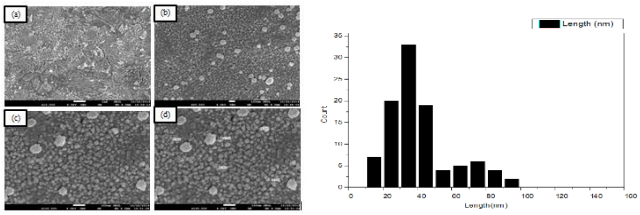

Figure 8. Surface morphology and particles size histogram of 10 wt% Mg doped ZnO thin films deposited on Al foil with different magnification and spin rate of 2000 rpm (a) 10kx (b) 50kx (c) 100kx

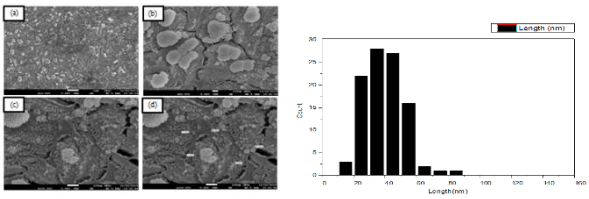

Figure 9. Surface morphology and particles size histogram of 15 wt% Mg doped ZnO thin films deposited on Al foil with different magnification and spin rate of 2000 rpm (a) 10kx (b) 50kx (c) 100kx

Piezoelectric Properties Analysis

The piezoelectric properties analysis was conducted by using ultrasonic vibrator and multimeter. Piezoelectric material was able to generate electricity when stress is applied. The vibration generates by the ultrasonic cleaner produced a potential difference for each sample. The potential difference of Mg doped ZnO thin film with different Mg contents and spin rate was summarized in Table 3. The value of potential difference increased, the resistivity value also increased as the Mg contents increased. According to previous work, Mg incorporated in ZnO crystals not only increased the grain boundary area to form electrical barriers and carriers dispersion but also reduced oxygen defects as the Mg-O bond has a more ionic character than the Zn-O bond, which reduced the concentration of electrons and increased resistivity at the same time [8]. The potential difference value increased as the spin speed increased. The film thickness will be thinner when fabricated at the higher spin speed causes the area of thin films to become larger. In spin coating, rapid solvent evaporation causes rapid molecular aggregation, which often induces the lattice strain in the grown film. In some situations, the metastable phase will appear in the film, making the molecular orientation desirable for charge transport [8].

Table 3. The potential difference of MgZnO thin film with different Mg contents and spin rate.

Samples	Potential Difference (V)
02000	0.056
52000	0.2549
52500	0.3095
53000	0.4314
102000	0.4433
152000	0.4919

CONCLUSION

Conclusively, using sol-gel spin coating techniques, pure ZnO and doped with different Mg content and spin rate rotation were successfully synthesized. The effect of Mg doped ZnO has been studied on it structural and physical properties. XRD analysis results with diffraction phases of the crystal plane of (101) representing ZnO phases while (220) for MgO phases respectively. Besides, FESEM reveals that thin film composition is spherical inhomogeneous nanoparticles with an average range of 20 to 60 nm. Other than that, Mg doped ZnO transmission spectroscopies showed that Mg doping in ZnO improved the UV wavelength transmission. Doping also raised the zinc oxide bandgap for the 15 wt% sample. PL spectra demonstrate the emitted electron at two emission bands: UV range (~370 nm) and visible range (~584 nm) for all samples. Mg doping also increased potential differences in term of piezoelectric properties. The results obtained by changing spin speed shows 5 wt% Mg doped ZnO fabricated with 3000 rpm has better results in term of characterization FESEM, UV-Vis, PL and piezoelectric properties since it has good surface morphology with uniform and dense distribution of nanoparticles, large optical bandgap energy, low intensity of PL peaks and higher potential difference among 52000 and 52500. For photonic application, the 52000 sample has the best result in PL characterization since it has the highest intensity of peaks. Moreover, 152000 samples show the best results in changing Mg concentration since it has the highest intensity of crystallite peaks, larger optical band gap energy, lower intensity of PL, and higher potential difference among the other concentration of Mg content.

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