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The effect magnesium (Mg) on structural and optical properties of ZnO:Mg thin film by sol-gel spin coating method

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The effect magnesium (Mg) on structural and optical properties of ZnO:Mg thin film by sol-gel spin coating method

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Abstract. ZnO:Mg thin film had been synthesized by sol-gel spin coating method. The materials used were zinc acetate dehydrate, magnesium, isoprol as a solution and diethanolamine as stabilizer. Concentration variation between Mg doped ZnO were 0.5; 1.0; 1.5; 2.0 and 2.5%. The XRD results showed that all samples were wurtize hexagonal with the smallest size of 24 nm for Mg doped of 0.5% and the biggest size of 28 nm for Mg doped of 2.5%. The SEM results showed that the ZnO:Mg thin film morphology was uniform and granules. The UV-Vis results showed the biggest transmission and absorbance values were in the range of 310 - 420 nm, and band gap of 3.155 - 3.217 eV.
Keywords: ZnO:Mg thin film, magnesium, doped, Sol-gel Spin Coating.

1. Introduction

Zinc Oxide (ZnO) is n-type semiconductor and belongs to II-VI compound offers an alternative to TiO_2 since it has band gap of 3.37 eV and binding energy of 60 meV at room temperature [1]. ZnO has emission that close to UV ray, photocatalyst, optical and electrical properties [2]. Recently the ZnO thin film has gain interest due to its advantage properties that can be applied in many areas such as gas sensor, solar cell, piezoelectric, light emitting diode and surface acoustic wave [3-6].

Doping is the addition of other atom into an element or compound by purpose in order to improve or to modify the properties of the compound or element. In this semiconductor technology doping and crystal defect are combined in order to control electrical conductivity, optical property, magnetic property, and other physical properties [7]. The addition metal doped into ZnO precursor solution will control the synthesis process systematically [8]. In order to improve the ZnO physical properties such as optical and electrical properties it is common to dope with metals from group IIIA periodic table such as B, Al, Mg, Ca, Cd and Ga [9-11]. In choosing the doper the radius of the doper need to be equal with the doped elements in order to produce compound with small distortion. The radius of Mg^{2+}(0,57 A) ion is comparable with the radius of Zn^{2+}(0,60A) ion, that make magnesium is suitable as a doper element to replace Zn in its lattice, and facilitate of boarding the band gap in Untraviolet region [12,13].

The synthesizing techniques are strongly affecting the structural and optical properties ot the ZnO thin film. Several synthesized methods have used in order to improve the quality of the ZnO thin film such as *molecular beam epitaxy* [14], *RF magnetron sputtering* [15], *pulsed laser deposition* [16], *spray pyrolysis* [17], *chemical bath deposition* [18], *physical vapor deposition* [19], dan *sol-gel dip coating* [5] and *sol-gel spin coating* [20]. In this research sol-gel spin coating method had been used in the synthesizing the ZnO thin film due to some advantages compared to other synthesizing methods. This method is realtively low cost, does not need big space, do not need high vacuum. In addition homogeneity, its composition, its thickness con be controlled and has a good microstructures [21].

2. Eksperiment

The synthesis of the ZnO:Mg thin film was sol-gel spin coating method. Materials used were Zinc Acetat Dehydrate as precursor, magnesium (Mg) as doper, isopropanol as solution and diethanolamine (DEA) as stabilizer. The ratio of Zinc Acetat dehydrate {Zn(CH3COOH).2H2O} and magnesium (Mg) 0,5; 1,0; 1,5; 2,0 and 2,5 %. This mix then was diluted in isopropanol solution, stir with magnetic stirrer for 10 minutes and gradually 1,72 ml Diethanolamine (DEA) was dropped into solution. The ratio DEA and ZnAc was 1:1. Then, the solution on the form of gel was dropped on a surface of FTO glass substrate that spinning with speed of 5000 rpm. Then, the samples was annealed to 2500C (pre-heat) for 5 hours continued with further annealing to 500oC (post-heating) for 5 hours. The ZnO:Mg thin films were characterized using XRD, SEM and UV-Vis.

3. Result and Discussion

3.1. Structure of the ZnO:Mg thin film

The diffraction pattern of XRD spectrum of ZnO:Mg thin film with Mg concentration of 0.5; 1.0; 1.5; 2.0 and 2.5% is shown in Figure 1. This spectrum show that all samples have crystal planes of (013),(110) d (11and2), and grown toward (112) plane. According to JCPDS 80-0075 card, these samples have hexagonal wurtzite structure. This results show that structure of the ZnO are unchanged with the Mg doping.

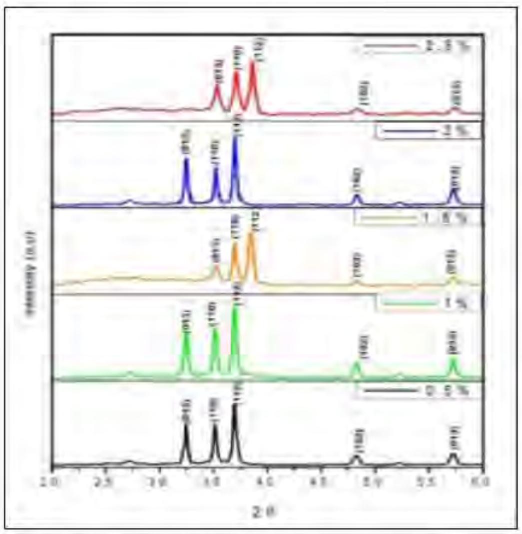

Figure 1. X-ray diffraction spectra of ZnO:Mg

The size of ZnO:Mg thin film was calculated by Scherrer equation [22]:

$$D = \frac{0{,}9\,\lambda}{\beta\cos\theta} \qquad (1)$$

where D = crystal size, λ= wavelength, β = *FWHM* (*full width half maximum*), θ = diffraction angle.

Table 1. Crystal size of ZnO:Mg

Sample Doping Mg (%)	Phase	Peak		Crystal size (nm)
		2θ (degree)	FWHM(degree)	
0.5	ZnO:Mg	36,9385	0,34740	24
1.0	ZnO:Mg	36,9440	0,34100	25
1.5	ZnO:Mg	38,4584	0,32680	26
2.0	ZnO:Mg	36,9639	0,33550	24
2.5	ZnO:Mg	38,4063	0,30930	28

Table 1 shows the size of ZnO:Mg thin film calculated using equation 1. It can be shown that the sizes of the ZnO:Mg thin films are generally increasing, especially when the number of the Mg was increased to 2.5 %. The increase in this size may be due to the gradation in crystal quality, crytsl distortion, and crystal defects. It was also found that the increase of magnesium concentration, increase the crystal size [23]. Magnesium is a suitable doper for ZnO thin film since it can replace Zn in the crystal lattice, and facilitate the broader of the bend gap in the ultraviolet region where the radius of Mg^{2+}(0,57 A) ion and Zn^{2+}(0,60A) ion are comparable [12,13].

Morfologi of ZnO:Mg thin film
The growth process of the Proses ZnO:Mg thin film can be depicted by the SEM image given in Figure 2.

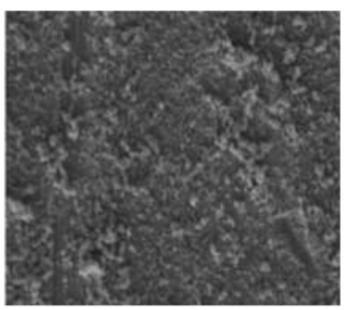

Figure 2. SEM image of ZnO:Mg thin film

The image shows the distribution of round un homogeny size of granules crystals coating the surface of the glass substrate without showing cracks, almost no pores and the border between granules cannot be seen. The smaller granules have sufficient *driving force* to undergo diffusion to form bigger granules. Inter diffusion of granules can cause necking that make the border between granules narrower and the surface of the ZnO:Mg thin film becomes smooth.

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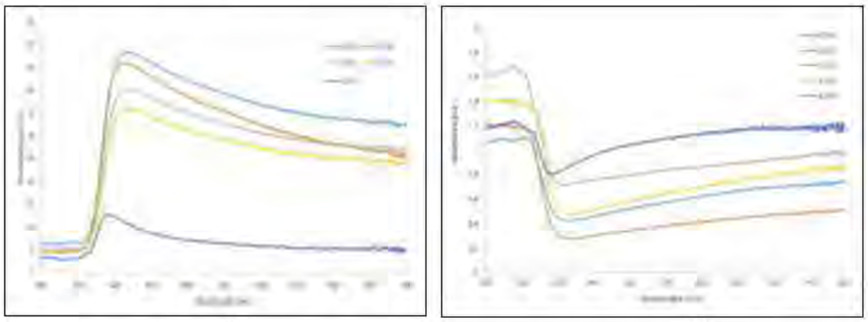
3.3. Optical property ot the ZnO:Mg thin film



(a) (b)

Figure 3. The UV-Vis of ZnO:Mg thin film (a) transmittance, (b) absorbance

The transmission and absorbance spectrum for all samples were taken in the range of 300-800 nm wavelength in order to analyze the application of the ZnO:Mg thin film for solar cell. Figure 3a transmission spectrum of the ZnO:Mg thin film. The spectrum shows sharp increase in transmission in the wavelength range of 310 – 420 nm due to the increase in the magnesium doping [10]. The decrease in transmission value due to lattice defect that can cause photon scattering [23]. The high transmission of ZnO thin film can be applied for solar cell [24]. The absorbance spectrum of the ZnO:Mg thin film is shown in Figure 3b. There is sharp decrease in absorption values for all samples in the range of 310 – 420 nm wavelength which are in the area of ultraviolet region and the increase of magnesium concentration shifts the absorption value to the smaller wavelength.

The relation between absorbance and photon frequency for a direct band gap semiconductor is given by the following equation [25[:

$$(\alpha h\nu)^2 = C_D(h\nu - E_{opt}) \qquad (2)$$

The variation of band gap of ZnO:Mg thin film and Mg doping concentration is determined by Tauc Plot Method is given in figure 4.

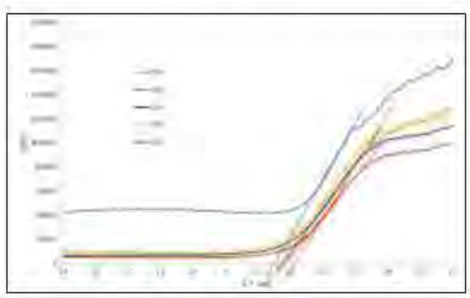


Figure 4. Band gap of ZnO:Mg versus Mg concentration using *Tauc Plot* method.

Table 2. Band gap of thin film ZnO:Mg

Sample	Band gap (eV)
ZnO:Mg 0,5%	3.185
ZnO:Mg 1,5%	3.217
ZnO:Mg 1,5%	3.178
ZnO:Mg 2,0%	3.170
ZnO:Mg 2,5%	3.155

The band gap of ZnO:Mg versus Mg doped concentration of Figure 4 is given in Table 2. This table shows the band gap increases as the Mg concentration increase from 0.5 % to 1.0 %, then decreasing as Mg concentration increasing from 1.5 % to 2.5. The increase in the Mg doped concentration is related to quality of the crystal. The increase in the Mg doping is likely produces crystal lattice distortion and lattice defects. In addition a rough surface of the ZnO:Mg thin film causing scattering rays. This makes as the thin film absorbs visible light and also due to blue-shift phenomenon [26,27].

4. Conclusion

The magnesium doped ZnO (ZnO:Mg) thin film had been successfully synthesized by *sol-gel spin coating* method. ZnO:Mg thin films have a wurtzite hexagonal structure with size of range 24 – 28 nm. The morphology of the ZnO:Mg thin film consists of an almost homogeny in rounded granules. The transmission and absorbance values are in the range of 310 nm to 420 nm wavelength. The band gap of the ZnO:Mg thin films is in the range of 3.155 to 3.217eV.

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