The Effect of Spin Coating Speed on Structural and Optical Properties of ZnO and ZnO/Dye Thin Films Synthesized by Sol-Gel Spin Coating Method

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Abstract. The ZnO thin films were successfully synthesized using sol-gel spin coating method. The surface other ZnO thin film then were coated with natural dye. Materials used were zinc acetate dehydrate, isopropanol, Diethanolamine and purple heart flower consecutively as based materials, solution, stabilizer, and dye. The ZnO thin films were grown glass by dropping Sol-gel on a surface of FTO glass with spin coating speed variation of 2000, 3000, 4000, and 6000 rpm. The ZnO thin films then successively pre-heated and pot-heated at 250°C and 550°C for 5 hours and holding time of 30 minutes. The source of the dye is boat lily flower was cut into small pieces and put into beaker glass. The sample then crushed with mortar and then milling until it becomes soft. Further, the extract was obtained by immersing it in aquadest, acetate acid, and ethanol with maceration technique. The ZnO thin films then immersed in an extract of dye solution for 24 hours to obtain ZnO/dye thin film. The XRD analysis shows that ZnO thin film size of within 26.5 – 36.9 nm. The optical properties of the ZnO and ZnO/Dye thin films were characterized using UV-Vis spectrometer. The UV-Vis spectrometer results show that there are variations of the ZnO thin film transmission as a result of spin coating speed of the Sol-gel spin coating method. The transmission of ZnO/dye thin films is higher than ZnO thin film and the absorbance of ZnO is higher than ZnO/dye thin films. The band gaps of the ZnO and ZnO/dye thin film were consecutively ranged 3.27 – 3.34 eV and 3.02 – 3.21 eV.

Keywords: sol-gel, spin coating speed, ZnO/dye thin films, structural, optical properties.

1. Introduction

ZnO thin film recently has gain interest among researchers due to its potential applications electrical optical devices such as sensor, nanodevice, and solar cell. The ZnO thin film has properties of near UV light emission, high conductivity and transparent, and photocatalyst[1]. ZnO is an n-type semiconductor that belong to a II-IV compound, it has band gap of 3.37 eV and bond excitation energy of 60 meV at room temperature [2-5].

The ZnO thin film can be synthesized by various techniques such as molecular beam epitaxy [6], RF magnetron sputtering [7], pulsed laser deposition [8], spray pyrolysis [9], chemical vapor deposition [10], and sol-gel spin coating [11]. The sol-gel spin coating method has several advantages...
such as cheap, does not require high vacuum, homogeneous composition, controllable thickness, and good microstructure [12].

The researches on ZnO thin film using sol-gel spin coating method with different variables have been conducted by several researchers during the past few years such as temperature variation of preheating [13] where it was found that the smallest crystal size is at pre-heating temperature of 250°C and the biggest energy gap was at 350°C, temperature variation of post-heating [14] where it was found that the smallest crystal size was at temperature of 400°C and the biggest energy gap was at temperature of 450°C. Other works try to improve the ZnO thin film by varying the precursors [15] where it was found that the crystal size decreasing as the spin coating speed increasing and the band gap increasing as the spin coating speed increasing. Therefore, in this work we try to improve the quality of the ZnO thin film by synthesizing the ZnO using sol-gel spin coating by increasing the temperature range from 2000, 3000, 4000, 5000, and 6000 rpm. Therefore, in this work we try to find the synthesis window to obtain optimum properties of the ZnO thin film that will used to build ZnO thin film based Dye Sensitized Solar Cell (DSSC).

2. Experiment

The ZnO thin films were synthesized by using Sol-Gel Spin Coating method. Materials used were zinc acetate dehydrate, isopropanol and diethanolamine(DEA) which were successively used as based material, solvent, and stabilizer. Acetate dehydrate \(\text{Zn(CH}_3\text{COOH).2H}_2\text{O}\) was diluted in an isopropanol solution with concentration of 0.8 M and then stirred with a magnetic stirrer for 10 minutes and little by little DEA was dropped into the solution to form gel. The gel then shed on to a surface of a FTO glass substrate and spinned with variation of 2000, 3000, 4000, 5000, and 6000 rpm. The samples then heated with pre-heating temperature of 250°C for 5 hours and post-heating temperature of 550°C also for 5 hours both with holding time of 30 minutes. The source of the dye is boat lily flower was cut into small pieces and put into beaker glass. The sample then further crushed with mortar and then milling until it becomes soft. Further, the extract was obtained by immersing it in aquadest, acetate acid, and ethanol with maceration technique. The ZnO thin films then immersed in an extract of dye solution for 24 hours to obtain ZnO/dye thin films.

The dye ZnO thin films then were characterized a UV-Vis spectrometer to determine the best optical properties. The dye-coating ZnO thin films were made by dipping the ZnO thin film into natural dyes solution with the ZnO thin films facing up for 24 hours to let the dyes adsorbed by the film. The ZnO thin films were characterized by using XRD UV-Vis, and ZnO/dye thin films were then characterized using UV-Vis.

3. Result and Discussion.

3.1. The ZnO Thin Films Structure

The diffraction pattern of the XRD measurements with spin speed variation are shown in Figure 1. The XRD analysis using search march, consecutively for spin speed of 2000, 3000, 4000, 5000 and 6000 rpm, show that all samples have the same pattern which miler index of (100), (002) and (101) peak at (101) plane. This result shows that all samples are ZnO thin film. The lattice parameters, consecutively for spin speed of 2000, 3000, 4000, 5000, and 6000 rpm, are \(a = 3.1950\ \text{Å}, \ c = 5.1120\ \text{Å}\); \(a = 3.1950\ \text{Å}, \ c = 5.1070\ \text{Å}\), \(a = 3.1950\ \text{Å}, \ c = 5.10273\ \text{Å}\) and \(a = 3.1950\ \text{Å}, \ c = 5.1027\ \text{Å}\) and hence the \(c/a\) ratio are successively 1.6; 1.59; 1.59; 1.59 and 1.59. These results show that the \(c/a\) ratio is in accordance with an ideal value of hexagonal cell which is 1.60 [17,18]. This result shows that all crystals are wurtzite hexagonal with the growth direction along with c-axis perpendicular with the surface of glass substrate in accordance with ZnO standard data card (JCPDS 80-0075).
Figure 1. X-ray diffraction spectra of ZnO

The crystal size of the ZnO thin films were calculated using Scherrer equation [19]:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

where \( D \) = crystal size, \( \lambda \) = wavelength, \( \beta \) = FWHM (full width half maximum), \( \theta \) = diffraction angle.
Table 1. Crystal size of ZnO

| Spin Coating Speed (rpm) | Phase  | 2θ (degree) | FWHM (degree) | Crystal size (nm) |
|-------------------------|--------|-------------|---------------|------------------|
| 2000                    | ZnO    | 34,5149     | 0,26910       | 36,9             |
| 3000                    | ZnO    | 36,9618     | 0,30640       | 27,4             |
| 4000                    | ZnO    | 36,9580     | 0,31600       | 26,5             |
| 5000                    | ZnO    | 36,9640     | 0,28000       | 29,6             |
| 6000                    | ZnO    | 36,9503     | 0,24730       | 33,9             |

Table 1 shows that the crystal size decreasing with increasing in spin coating speed of 2000, 3000, 4000 rpm but it increases as the spin coating speed increases from 4000, 5000, 6000 rpm. This result shows that the spin coating speed can modify the growth of the ZnO thin film, the higher the spin coating speed the higher the centrifugal force to spread the gel on the glass surface to form the ZnO thin film. The same result was also found by Ilican et.al [16] who found the smallest crystal size at spinning speed of 3000 rpm, and Ajadi et.al. [20] at spinning speed of 4000 rpm and duration of spinning of 40 seconds.

3.2. Optical Properties of The ZnO and ZnO/Dye Thin Film

The transmission and absorbance spectrum for all samples taken at the range of 300 – 800 nm in order meet its application in solar cell. The ZnO thin film transmission is shown in Figure 2(a). It shows that the highest transmission is 41.3 % at the spinning coating speed of 2000 rpm and the lowest is 25.9 % at the spin coating speed of 4000 rpm. The transmission spectrum of the ZnO/dye thin films were shown in Figure 2(b). The Figure shows that the highest transmission value is 44.799 % at 3000 rpm spin coating speed and the lowest transmission value is 25.135 % at 4000 rpm spin coating speed. This indicates that there is the coating of natural dye increase the transmittance value of the ZnO thin films.

![Figure 2](image-url)

Figure 2. The transmission spectrum of: (a) ZnO thin films, and (b) ZnO/dye thin films.

Figure 3(a) shows the highest absorption value is 2.38 a.u at the spinning coating speed of 4000 rpm and the lowest at 0.95 a.u at the spin coating speed of 2000 rpm. Figure 3(b) shows the highest absorption value is 1.77 a.u at the spin coating speed of 4000 rpm and lowest absorption value is 0.86 a.u at the spin coating speed of 2000 rpm. According to spin mechanism, the higher the spin coating speed the higher is the centrifugal force that affecting the decrease in the absorbance of the ZnO thin film [18].
Figure 3. The absorption spectrum of: (a) ZnO thin films, and (b) ZnO/dye thin films.

The band gap of both ZnO and ZnO/dye thin films as a function of spin speed coating are shown in table 2. The band gap variation as a result of variation in the spin coating speed in the synthesis of the ZnO thin film based on Figure 6 is given on Table 2.

Table 2. The band gap of ZnO and ZnO/Dye thin film

| Spin Coating Speed (rpm) | ZnO Band Gap (eV) | ZnO/Dye Band Gap (eV) |
|--------------------------|-------------------|-----------------------|
| 2000                     | 3.34              | 3.21                  |
| 3000                     | 3.32              | 3.13                  |
| 4000                     | 3.29              | 3.02                  |
| 5000                     | 3.30              | 3.06                  |
| 6000                     | 3.27              | 3.11                  |

The effect of spin coating speed on the ZnO thin film band gap is shown in Table 2. The table shows there is a decrease in the band gap as the spin coating speed increases from 2000 rpm to 4000 rpm, however as the it increases from 4000 rpm to 5000 rpm followed by decreasing at 6000 rpm. This may be due to the increase in the centrifugal force [16]. In addition, the increase of spin speed coating resulting inhomogeneous sol gel droplet on the surface of the FTO glass substrate and as it is heated, the band gap is decrease. The band gap of ZnO/dye thin film is slightly smaller than the band gap of ZnO thin film. This is may be due to the increase in the thin film thickness.

4. Conclusion

The ZnO thin films, with variation of spin coating speed (2000, 3000, 4000, 5000 and 6000 rpm), have successfully synthesized by sol-gel spin coating method. The ZnO thin films have wurtzite hexagonal structural with crystal sizes between 26.5 – 36.9 nm. The band gap values are within 3.27 – 3.34 eV. The band gap of ZnO/dye thin films is slightly smaller than the band gap of ZnO thin films.

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