The Effect of Post Annealing Time on Structural and Optical Properties of ZnO Thin Films by Sol-Gel Spin Coating Method

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Abstract. ZnO thin film has been synthesized by sol-gel spin coating method. The materials used were zinc acetate dehydrate as a basic material, isopropanol as a solution and diethanolamine as a stabilizer. The ZnO thin films were grown on FTO conductive glass substrate and post annealed at 500°C with annealed time consecutively 30, 60, 90, 120 and 150 minutes. The XRD results show that the crystal structure is wurtzite hexagonal with size of 22 nm for 30 minute annealing time. The SEM results show a uniform homogeneity round granules. UV-Vis measurements show a sharp transmission values and the decrease in their absorbance for all samples in the range of 310 to 430 nm wavelength. The band gaps are within 3.073 - 3.140 eV.

Keywords: ZnO thin film, post annealing time, Sol-gel Spin Coating.

1. Introduction
Zinc Oxide is an n-type semiconductor material with band gap of 3.37 eV and binding energy of 60 meV at room temperature [1,2]. ZnO has a good optical, electrical and piezoelectric [2]. These properties make the ZnO gain attractive applications such as luminescence, laser diode, solar cell, gas sensor and optoelectronics [3 – 5].

Thin films can be made of organic, non-organic, metal, mix metal-organic that can have conductor, semiconductor, and insulator properties. Recently the ZnO thin film technologies have developed such as molecular beam epitaxy[6], RF magnetron sputtering[7], pulsed laser deposition[8], spray pyrolysis [9], chemical bath deposition[10], physical vapor deposition[11], dan sol-gel dip coating [2] and sol-gel spin coating[12].

In this research the ZnO thin films were grown using sol-gel spin coating by varying annealing time. This sol-gel spin coating method is relatively simple, effective, low cost, does not need big space, does not need high vacuum. Moreover, it can produce homogeneity, controllable thickness, and has good microstructures [13].

2. Eksperiment
The ZnO thin films were synthesized by sol-gel spin coating method. The materials used were Zinc Acetat Dehydrate, isopropanol and diethanolamine (DEA) consecutively as basic ingredient, solution, and stabilizer. Zinc Acetatdehydrate {Zn(CH₃COOH).2H₂O} was diluted in isopropanol, stirred with magnetic stirrer and after 10 minutes 1.72 ml gradually put into DEA. The ratio between DEA danZnAc was 1:1. The solution in the form of gel is then dropped on the surface of FTO glass
substrate with spin coating of 5000 rpm speed. The sample then was heated gradually until it reached 250°C for 5 hours and kept at the temperature for 30 minutes for pre-heating, the temperature then gradually increased to 500°C for post-heating temperature and kept in the variation each of 30, 60, 90, 120 and 150 minutes. All the samples were characterized using XRD, SEM, and UV-Vis.

3. Result and Discussion

3.1. The ZnO thin film crystal structures

The diffraction patterns of the XRD of ZnO thin film samples with post annealing variations of 30, 60, 90, 120, and 150 minutes are given in Figure 1. Diffraction patterns show that all samples have (100), (002) and (101) planes, and the highest peak is (101). These show that the crystal has wurtzite hexagonal structure as shown in the data card of JCPDS 80-0075 of ZnO.

![Figure 1. X-ray diffraction spectra of ZnO](image)

The size of the ZnO crystal was calculated by using Scherrer equation [14]:

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $D$ = crystal size, $\lambda$ = wavelength, $\beta$ = FWHM (full width half maximum), $\theta$ = diffraction angle.

| Sample of post annealing time (minutes) | Phase | $2\theta$ (degree) | FWHM (degree) | Crystal size (nm) |
|----------------------------------------|-------|--------------------|---------------|-------------------|
| 30                                     | ZnO   | 36,9775            | 0.37500       | 22                |
| 60                                     | ZnO   | 36,9513            | 0.30490       | 27                |
| 90                                     | ZnO   | 36,9582            | 0.32640       | 27                |
| 120                                    | ZnO   | 36,9545            | 0.33760       | 25                |
| 150                                    | ZnO   | 36,9428            | 0.33900       | 25                |
The sizes of the ZnO thin film crystal using equation 1 is shown in Table 1 slightly vary from 22 to 27 nm, where the smallest size is 22 nm, when the holding time of 30 minutes. The result shows that the increase in holding time during the post-heating only make the crystal size slightly bigger which probably due to incorporation of other elements. The growth of ZnO thin fil crystal was affected by post-heating temperature, since the highest the post-heating temperature the higher the energy of the atoms to form the crystal [15,16].

3.2. ZnO thin film morphology
The growth process or the ZnO thin film was determined by SEM images as shown in Figure 2. The images show that ZnO thin films have a high density of small round granules. The images also shows that there is no clear border between granules and the sizes of the granules are not uniform. Atoms of the smaller granules have a sufficient driving force to form bigger granules. The diffusion among granules will form necking that causes the border among the granules will be smaller and make the film surface become smooth.

![Figure 2. SEM image of thin film ZnO](image)

3.3. Optical properties of ZnO thin film

The transmission and adsorption UV-Vis spectra were taken in the range of about 300 – 800 nm which are in the range of solar cell application. Figure 3a shows transmission spectrum the ZnO thin film. The figure shows a sharp increase in transmission value in the range of 310 – 430 nm which is in the
ultraviolet to visible light range. The highest and the lowest transmissions are consecutively at holding time during post-heating 30 and 120 minutes. According to heating mechanism the longer the holding time will let the compression of a bunch of powder and a strong bond between granules and pores between granules. The absorbance spectrum of the ZnO thin film is shown in Figure 3b. It shows a sharp decrease in absorption for all samples in the wavelength range of about 310 – 430 nm. The lowest and the highest absorptions are, at the holding time during post-heating, 120 dan 30 minutes. This absorption range is also in the visible light range and therefore is suitable for optoelectronic application [17].

Semiconductor that has a direct band gap, the relation between absorbance and photon frequency is given by the following equation [18].

\[(a\nu)^2 = C\nu(h\nu - E_{opt})\] (2)

The band gap of all samples with holding time variation, based on Tauc Plot method, is given in Figure 4.

![Figure 4. Band gap of ZnO thin film with various holding time.](image)

Table 2 shows the ZnO thin film band gap with variation of holding time based on Figure 4.

| Holding Time (minutes) | Band gap (eV) |
|------------------------|---------------|
| 30                     | 3.080         |
| 60                     | 3.125         |
| 90                     | 3.119         |
| 120                    | 3.140         |
| 150                    | 3.073         |

The highest and the lowest band gap are 3.140 eV and 3.073 eV for holding time during post-heating of 120 and 150 minutes. There are variations in band gap due to variation in holding time. There are considerable increase from 30 to 60 and 90 minutes holding times, and sharp increase at 120 minutes holding time, and decrease to almost the same as 30 minutes holding time at 150 minutes holding time. The increase in the band gap due to the decrease in the distance between granules and higher density of the particle granules[19-21]. However the decrease in the band gap, as the holding time increase further to 150 minutes, makes the agglomeration of particle.
4. Conclusions
The ZnO thin films with variation of holding time during post-heating have been synthesized by sol-gel spin coating method. All ZnO thin film samples have wurtzite hexagonal structure with crystal size in the range of 22 - 27 nm and with morphology of almost uniform round granules shape. The transmission and absorbance values are in the range of 310 to 430 nm wavelength. The band gaps are in the range of 3.073 - 3.140 eV.

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