Photoresponse on Nanostructure of ZnO Thin Films Prepared by Sol-Gel Spin Coating Technique

Amir Akmal b Md Shokor
NANO-ElecTronic Centre, Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia

***Abstract*—Zinc oxide (ZnO) thin films have been prepared by sol-gel spin coating method on glass substrate. ZnO thin films at different thickness were investigated. Optical properties measure from UV-Vis spectrophotometer shows the optical band gap increased when the thin film thickness increased. The surface roughness also increased as the thickness increased shows from atomic force microscopy (AFM) measurement. Field emission scanning electron microspcopy (FESEM) images reveal the increasing of porous among grains when the ZnO thin film increased. Current-Voltage (I-V) measurement result shows there is photo response characteristic on ZnO thin film when illumination state show higher conductivity than dark state.**

I. INTRODUCTION

The wide range of useful properties displayed by ZnO has been recognized for a long time. Now a day zinc oxide (ZnO) is the most common material used in commercial devices due to its low cost. ZnO is a versatile n-type semiconductor finding application from gas sensors, transparent conducting electrodes to short wavelength optoelectronics devices.[1] ZnO has the characteristic of a semiconductor with a wide direct band gap (3.44eV) and have a large exciton binding energy. This large exciton binding energy indicates that efficient excitonic emission in ZnO can persist at room temperature and higher. ZnO has a large piezoelectric constant which in piezoelectric materials, an applied voltage generates a deformation in the crystal and vice versa. These materials are generally used as sensors, transducers and actuators. ZnO also has a strong sensitivity of surface conductivity to the presence of adsorbed species which make the conductivity of ZnO thin films is very sensitive to the exposure of the surface to various gases. Other properties of ZnO are high thermal conductivity. High thermal conductivity translates into high efficiency of heat removal during device operation. One of the most attractive features of ZnO as a semiconductor is that large area single crystals are available. ZnO also observed that have a good radiation hardness. Radiation hardness is important for applications at high altitude or in space. [2] ZnO nanostructures had been discovered in various forms such as ZnO thin film, nanowires(NWs) [3], nanopores [4], nanorods [5], nanobelts [6],nanorings [7], nanocables [8] and nanotubes[9],nanocolumns [10], nanocombs [11] and nanoneedles [12]. There are many parameters to be studied in order to produce a good quality of ZnO thin film. One of them is to study on the electrical properties of the nanostructure ZnO thin film prepared by sol-gel spin coating method.

II. METHODOLOGY

The zinc oxide thin film was deposited on the glass substrate by sol-gel spin coating method. Zinc acetate dehydrate ($Zn(O_2CCH_3)_2 \cdot (H_2O)_2$), 2-methoxyethanol ($C_3H_8O_2$) and monoethanolamine ($C_2H_7NO$) (MEA) were used as starting material, solvent and stabilizer respectively. The glass substrate were cleaned in ethanol, methanol and deionized (DI) water for 10 minutes in ultrasonic water bath which is called as sonication process. The mixed solution are stirred at 60^0C for 3 hours before aging process which is stirred at temperature hours for a day. ZnO thin films were deposited on the glass substrate by sol-gel spin coating method. The precursor solution was dropped ten times onto the glass substrate, which were spin at 3000 rpm for one minute. After the spin coating process, drying process is applied to the films to evaporate the solvent and remove organic residuals. The films are dried at 150°C for 5 minutes. The spin coating and drying processes were repeated for 3, 5, 7 and 9 times to increase the samples thickness. Fig. 1 shows the flow chart which is showing the procedure for preparing the ZnO thin films. The effects of thickness on the optical and structural properties of ZnO thin film were reported by using the UV-Vis spectrophotometer and atomic force microscopy respectively.

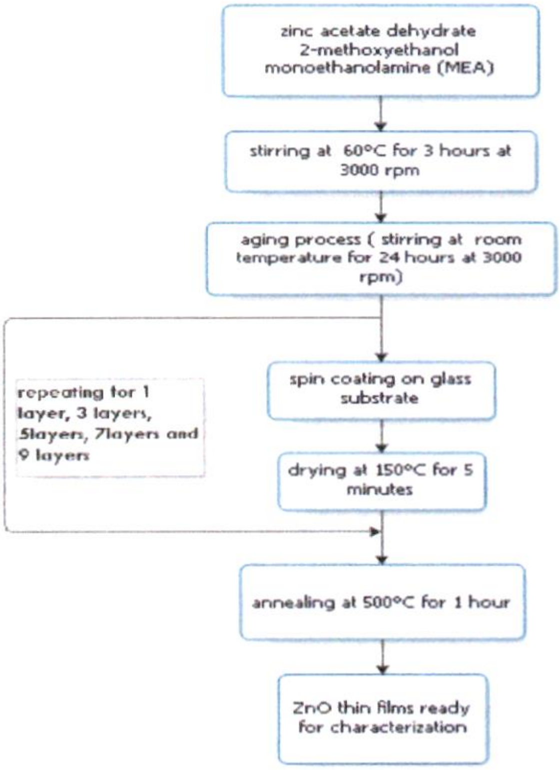


Fig. 1. Flow chart for preparing ZnO thin films

III. RESULTS AND DISCUSSION

layer	1st thickness (nm)	2nd thickness (nm)	3rd thickness (nm)	Average thickness (nm)
1	41.5	34.61	41.27	39.13
3	108.44	116.96	120.35	115.25
5	161.28	192.88	153.53	169.23
7	222.05	231.75	219.11	224.30
9	294.81	322.43	316.76	311.33

Table. 1. average thickness of ZnO thin films

The table 1 shows the average thickness of 5 different layers. The ZnO thin film thicknesses were measured by using the surface profile. Each layer was measured up to three times before obtaining the average thickness of the ZnO thin films.

A. Optical Properties of ZnO thin films

The optical transmittance spectra, absorption coefficient and optical band gap are shown on the Figure 2 and Figure 3 and Figure 4 respectively. The effects of increasing the ZnO thin films thickness are presented. The crystal structure and orientation of the ZnO thin film were investigated by UV-Vis spectrophotometer. Figure 2 represent the optical transmittance spectra against wavelength spectra of ZnO thin film with 5 different thicknesses. From this figure, the transparency of films become decreases as the increase of thickness and surface roughness. It is clear that all the sample have high transmittance in the whole visible range. This may be due to the decreased optical scattering caused by the decreased of grain boundary density owing to the increase of grain size. [13-17] From the above result, it can be known that ZnO thin films prepared by sol–gel method have high transmittance in the visible range.

Figure 3 shows the absorption coefficient against wavelength. The range for wavelength spectra is from 200nm to 1000nm. The absorption coefficient spectra obtained from UV-Vis spectrophotometer as shows in figure 3 shows that all different thickness sample have a low absorbance on visible light (390nm-700nm) and near infrared (IR) (700-1000nm) but have high UV (10nm-380nm) absorption properties. The band gap of ZnO is approximately 3.44eV [2] . The experimental results shows that the ZnO thin films can be excited by photon with wavelength around 300nm to 380nm. It shows the variance of absorption coefficient for the five different thicknesses. The strong energy of photon in UV region caused the excitation in electron from valence band to conduction band. Photon with sufficient energy enough which is higher or equal with band gap of ZnO can caused the excitation.

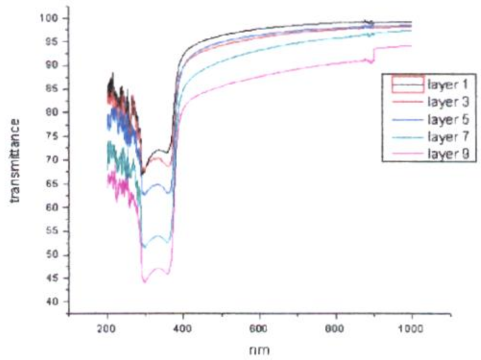


Fig. 2. optical transmittance of ZnO thin films at different thickness

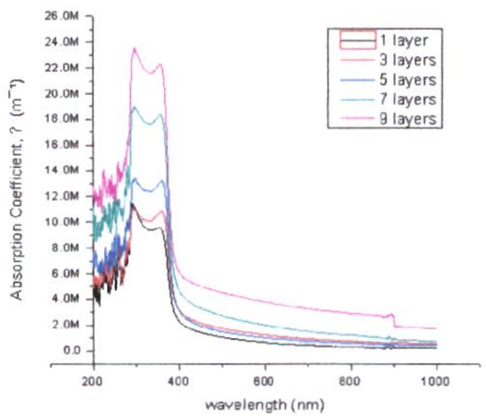


Fig. 3. absorption coefficient spectra of ZnO thin films at different thickness.

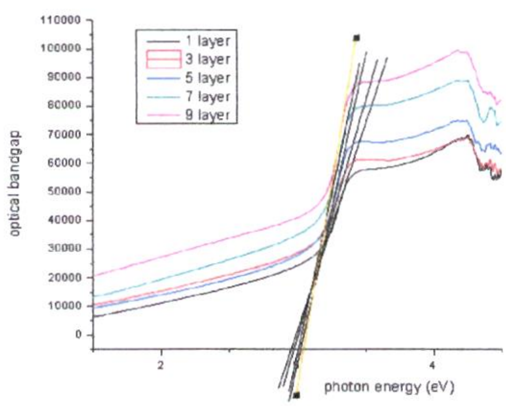


Fig. 4. Optical band gap of ZnO thin film with different thickness.

The optical band gap as shown on Fig. 4 were obtain from the measurements by plotting $(\alpha h\nu)^2$ against photon energy (eV). The optical band gap for all sample for ZnO thin films are found that increased when the thickness increasing. The less thick sample is found with smaller band gap which is 2.89eV. The highest band gap which is 3.11 eV when the thickness is at the thickest thin film which is 311.33 nm. The experimental result shows that sample with less thickness gives a smaller band gap which is good for electron excitation because the photon just required that amount of energy to excite from valence band to conduction band. Table. 3 below show the thin film thickness effects on the band gap.

No. of layer	Thickness (nm)	Band gap (eV)
1	39.13	2.89
3	115.25	2.95
5	169.23	3.06
7	224.30	3.00
9	311.33	3.11

Table. 3. The thickness and band gap of ZnO thin film at different layer.

B. Structural Properties of ZnO thin film

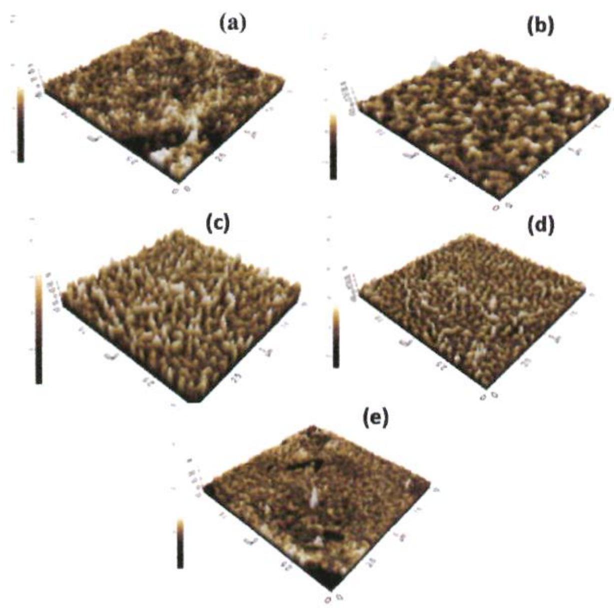


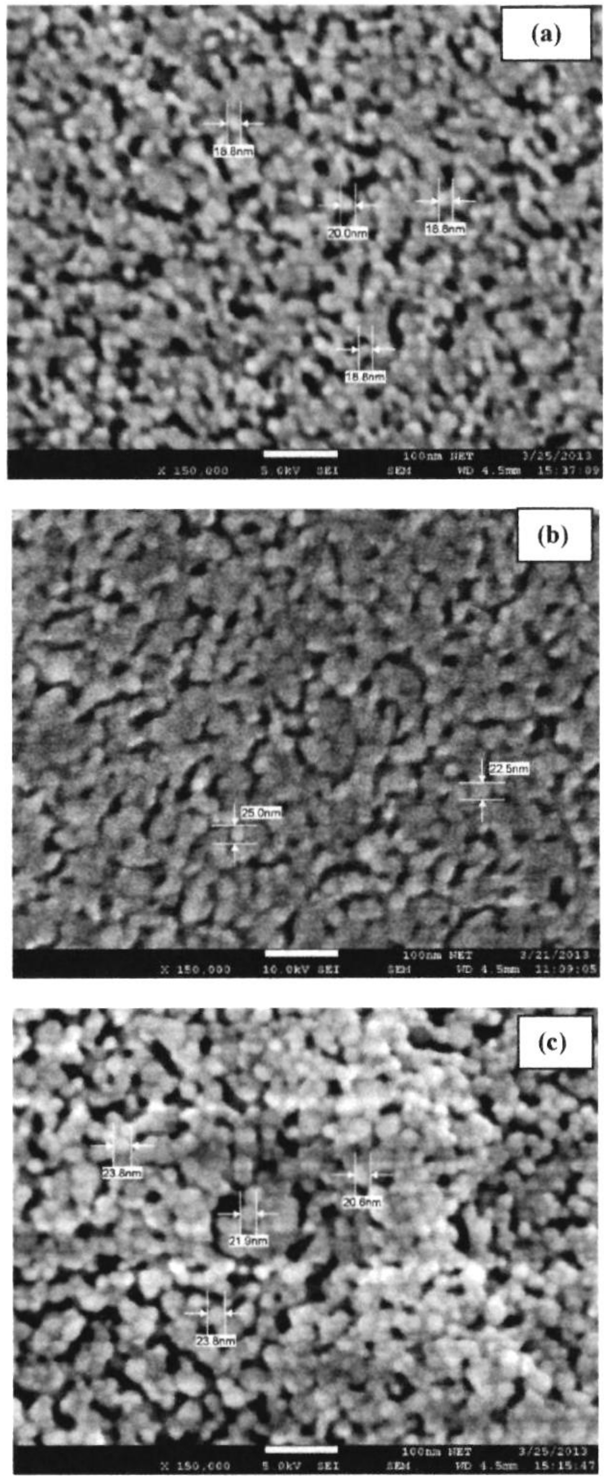
Fig. 5. 3 dimensional images from AFM for (a) 1 layer, (b) 3 layers, (c) 5 layers, (d) 7 layers and (e) 9 layers

Number of layers	mean roughness, Ra (nm)	Rms roughness, Rq (nm)
1	0.395	0.478
3	0.391	0.550
5	0.457	0.574
7	0.506	0.637
9	0.641	0.797

Table. 2. mean roughness and root mean square roughness of ZnO thin films

Figure 4 shows the 3 dimensional images from atomic force microscopy (AFM). Each image is from different layer which is different thickness. Annealing at the temperature of 500°C given the images the ZnO thin films. The surface morphology of the ZnO thin films shows there is increasing in mean roughness and root mean square roughness (rms) as the average thickness increasing. The experimental results in table 2 show that the ZnO thin films with average thickness of 39.13nm, the rms roughness is 0.478nm while the mean roughness is 0.395nm. Both type of roughness increasing for layer 3, 5, 7 and 9 layers. Increasing in surface roughness means the surface area also increasing. Therefore as the results show on the optical properties, the most thick ZnO thin films give the result with highest absorbance properties in UV region. Figure 3 also shows that the increasing of thickness in ZnO thin films decreasing the transparency and this is due to the increasing of surface roughness. [17-18]

Figure 5 below shows the FESEM images for ZnO thin films for all five different thicknesses. The images are 1 layer, 3 layer, 5 layer, 7 layer and 9 layer respectively. From the figure 5, it can be observed that ZnO thin films have high surface roughness on surface morphology as the thin films increasing. From the result, it shows that the grain size is in nanometer size. From the FESEM result, the porous between grains increasing when the thickness if ZnO thin film increased. [18-19]



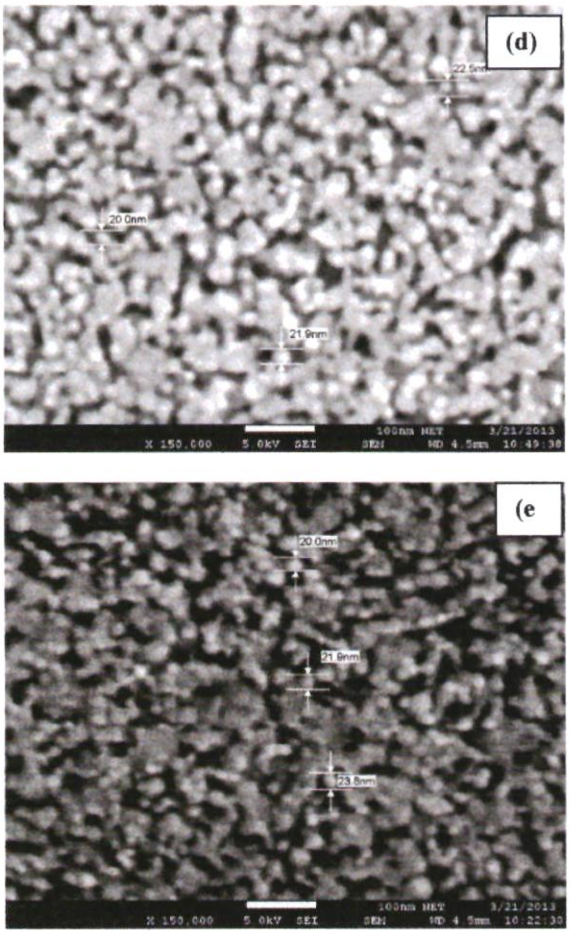


Fig. 5. FESEM images of ZnO thin films of (a) 1 layer, (b) 3layers, (c) 5 layers, (d) 7 layers and (e) 9 layers.

C. *Electrical Properties of ZnO thin film*

Fig. 6(a) and (b) shows the result of Current-Voltage measurement for ZnO thin film at (a) dark state and (b) illumination state. The result show an almost linear I-V curve obtained from the measurement meaning that all the example exhibit Ohmic behavior with Au metal contact. The result for both dark and light ambient state did not show much different in I-V characteristic. Therefore, the electrical behavior of ZnO thin film with respect of the thickness were examined through measurement of electrical conductivity.[19]

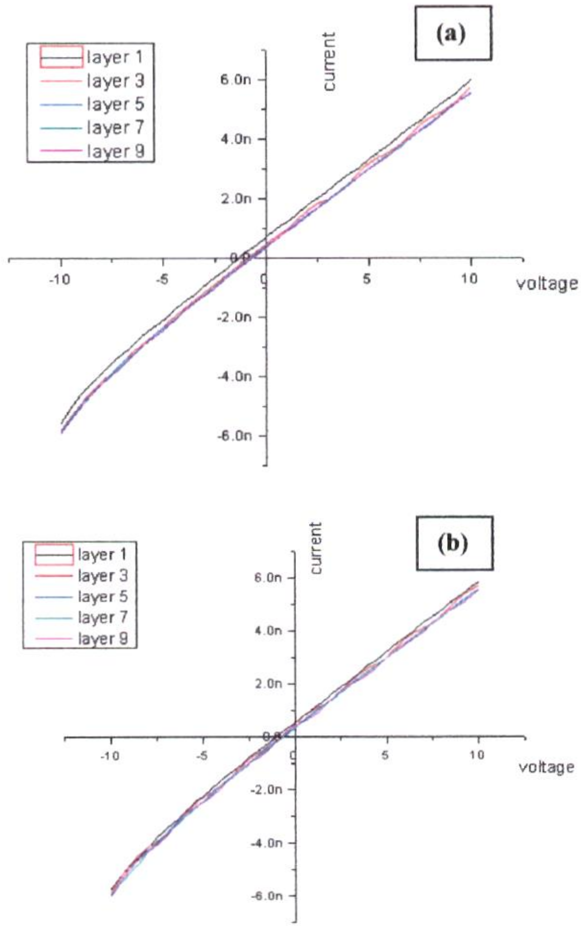


Fig. 6. I-V curve of ZnO thin film at (a) dark state and (b) at illumination state

Fig. 7. Show the conductivity of ZnO thin film for dark and with ambient light. The conductivity of ZnO thin film decreased when the thickness of the thin film increased. From the conductivity measurement, it shows that the ZnO thin have a photo response since the illumination state have higher conductivity than during the dark state.[19]

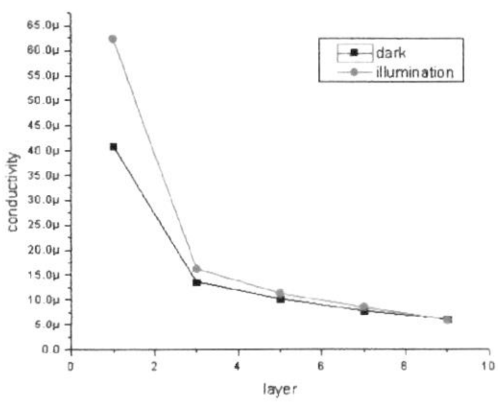


Fig. 7. Conductivity of ZnO thin film during dark and illumination state for different layer

IV. CONCLUSION

ZnO thin films with different thicknesses were prepared on glass substrate by using the sol-gel spin coating technique. The optical, structural and electrical properties of ZnO thin films have been investigated and it show that the increasing in ZnO thin films have effects on these properties. The experimental result from UV-Vis ZnO thin films shows that the optical bandgap increased when the thin film increased. AFM result shows the increasing in thickness also increasing the roughness on surface morphology of ZnO thin film. The FESEM images show the increasing of porous among the grains as the thickness increased. The conductivity of ZnO thin film found to be decreased when the thickness is increased.

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