Crystalline Size Effect on the Electrical Properties of Zinc Oxide Nano-Structured Thin Films for Solar Cell Applications

A.R. Zainun[1,]*, M.H. Mamat[1], and M. Rusop[1,2]

[1]*Solar Cell Laboratory, Faculty of Electrical Engineering;*
[2]*NANO-SciTech Centre, Institute of Science;*
Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia
**Email: ayib_rosdi@hotmail.com*

Abstract. The effect of crystalline size of ZnO thin film towards it electrical properties was conducted and studied. Through the process of sol gel method, ZnO solution was afforded by dissolving zinc acetate dehydrate as precursor into 2-methoxyethanol as solvent and added monoethanolmine as chelating agent. This solution was then deposited onto silicon substrates to produced thin film by spin coating technique. Following the work objective, produced thin film was sintered at different temperature to analyze it grain size against the properties of electrical. Scanning electron microscopy (SEM) was used to find any enhancement in grain size of ZnO. SEM results were supported with full width at half maximum (FWHM) values that proved the ZnO grain size improved with increasing temperature. For it electrical properties, current-voltage (I-V) measurement was conducted and it showed some progress in it results.

Keywords: Crytalline size effect; ZnO thin film; Electrical Properties; Sol-gel method
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INTRODUCTION

The electrical properties of a semiconductor material directly depend on the number of current carriers per unit volume, which is the concentration of carriers. The current carriers will be formed more when the heat energy by absorption of the precursor atom is released through breakage of a covalent bond and release of a free electron that carries the energy away. The electrons released from covalent bonds broken by thermal energy are mobile charged particles, so they can flow through the crystal to create electric current [1]. The smooth of current flow is depends on crystalline of the thin film produced. If the crystalline form uniformly in good shape, better current will flow and create more energy to be release.

In the case of ZnO, it is known as n-type semiconductor which is negatively charged free electrons and has a free-exciton binding energy of about 60 meV which is higher than Gallium Nitride (GaN) [2]. It is also a transparent semiconductor material which has been applied in various electronic devices application [3, 4, 5] and has several favorable properties such as good transparency, high electron mobility, wide bandgap and strong room-temperature luminescence [6].

Preparation of ZnO thin film had been done by various techniques before, but among them most utilized technique is spin coating method [13, 14] because it does not required expensive and complicated equipment. Furthermore, it provides good control in doping level, solution concentration, homogeneity and easy to be coated on the desired shape and area. Deposition by spin-coating method is able to produce uniform thin films on the substrates where the process involved dispersing an amount of solution onto the substrate that is rotated at high speed in order to spread the solution by centrifugal force.

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Unlike other techniques such as radio frequency (RF) magnetron sputtering [6], molecular beam epitaxy (MBE) [7], chemical vapor deposition (CVD) [8], reactive RF diode sputtering [9], direct current (DC) magnetron reactive sputtering [10], ionized cluster beam deposition (ICBD) [11] and pulsed laser deposition [12], the preparation of the equipment could be costly and complicated.

The electrical properties of ZnO thin film are strongly depended on some factors such as the crystallographic orientation, crystalline size and surface morphology. In this work, the effect of crystalline size of ZnO thin film to the electrical properties is studied based on some parameters changes such as solution concentration and sintered process since thermal energy factor is an important reason in increasing of free electrons.

EXPERIMENTAL

Zinc oxide solution was prepared by mixing zinc acetate dehydrate (ZnAC) as precursor and dissolved in 2-methoxyethanol. Monoethanolmine (MEA) was added into solution working as stabilizer to the mixed solution. Molar concentration of zinc acetate and MEA was fixed at 1.0 M. Transparent and homogenous solution was afforded by heated and stirred at 60 °C for 3 hr. Before used as coating solution in the deposition process, the solution was furthered aged at room temperature for 24 hr.

Silicon substrate was used to coat the ZnO thin film using spin-coating machine (LAURELL). The spin was run at 3000 rpm for 60s while dripping the solution 10 drops onto substrate. The coated substrate then was heated at 150°C for 10 minutes to evaporate solvent and eliminate organic component in the film. To increase the thickness of the thin film, dripping and heated procedures had done 10 times. These mean that one sample will have 10 layers. Above procedures were repeated to all samples. Each of the thin films were then sintered at 350, 400, 450 and 500°C respectively using Proterm furnace at room temperature.

To reveal the different of crystalline size, surface of thin films were examined using scanning electron microscope (SEM, JEOL JSM6360LA). The optical properties of ZnO thin films were characterized using UV-Vis-NIR spectrophotometer (Cary 5000). The electrical properties were studied using current-voltage (I-V) measurement system (Advantest R6243). The platinum (Pt)/gold (Au) contacts for I-V measurement were deposited using sputter coater (Polaron) at deposition current of 10 mA and deposition time of 90 s.

RESULTS AND DISCUSSION

The surface morphologies of ZnO thin film on Si substrate sintered at different sintering temperatures is shows in fig. 1. The SEM images show the thin films are uniform as the substrates were fully covered by ZnO particles. It also could be considered that the thin films prepared using 1.0 M solutions are dense for all sintering temperatures. Also, it is suggested that the particle merging activity occurred between adjacent ZnO particles as sintering process were introduced to improve the ZnO thin film crystalline at higher sintering temperature. Crack has also observed at temperature 450^{o}C due to the difference of thermal expansion coefficient between substrate and ZnO thin film [14] which result in thermal strain during sintering and cooling process.

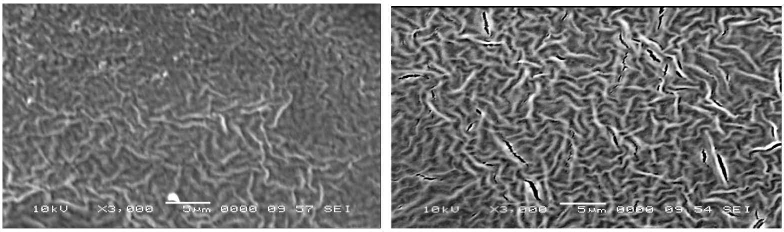

Fig. 1 SEM image of ZnO thin films deposited on Si substrate sintered at (a) 350 and (b) 450°C.

The full width at half maximum (FWHM) values as the function of sintering temperatures was shown in the table 1. It was found that the FWHM value decreased with sintering temperatures which also indicates the improvement of ZnO crystalline at higher sintering temperature. The grain size of the samples was calculated using Scherer's formula as indicated by following equation (1) [15]:

$$D = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

where D is grain size, λ is X-ray wavelength of 1.54 Å, B is full width at half maximum (FWHM) in radian and θ is diffraction angle. The calculation shows the increment of grain size with sintering temperatures as the result of the particle merging activity at higher sintering temperature.

Table 1: FWHM values and ZnO grain size at different sintering temperatures.

Sintering Temperature (°C)	FWHM Values at (101) Plane(°)	Grain Size (nm)
As Deposited	0.707	14
350	0.479	21
400	0.426	23
450	0.298	33
500	0.261	38

The optical absorbance spectra and properties of ZnO thin film with different sintering temperatures was taken in the wavelength region of 200-800 nm as in fig.2. It could be considered that the improvement in UV absorption properties of ZnO thin films occurred at higher sintering temperature. Such occurrence might due to the improvement of ZnO crystalline at higher sintering temperature as show in table 1 of FWHM which also improves the UV absorption properties of ZnO thin films.

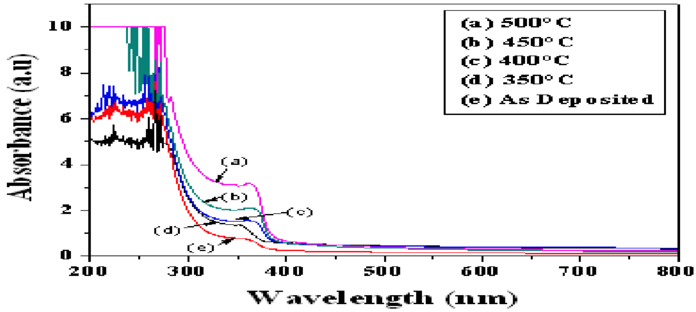

Fig. 2: Optical absorbance spectra of ZnO thin films at different temperatures.

The current- voltage (I-V) curve measurement of ZnO thin films at different sintering temperatures measured using 2 probes and power supply system at room temperature under room illumination as show in fig. 3. Pt/Au metal contacts were used as electrodes for the measurement. The results exhibited Ohmic behavior at all films with the Pt/Au electrodes as linear curve.

The result also shows the improvement in ZnO thin film electrical properties with sintering temperatures. The improvement in electrical properties of ZnO thin film at higher sintering temperature might due to the better crystalline properties which increase the conductivity of ZnO thin films. It has been reported that sintering process induces the increment of carrier concentration as well as electron mobility which enhance the electrical properties of ZnO thin films [6]. However, the I-V curve for sample sintered at 400°C is lower than samples sintered at 350°C possibly due to crack area which disturb the electron mobility in the thin films.

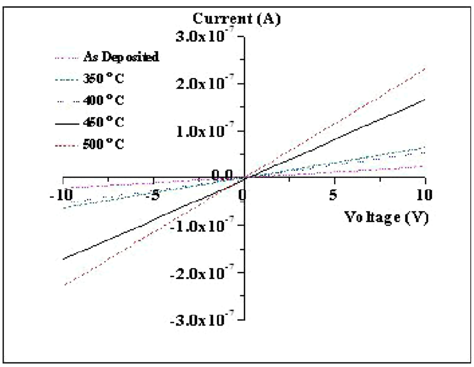

Fig. 3: Electrical properties of ZnO thin film at different temperatures.

CONCLUSION

ZnO thin films were prepared on silicon substrate by the sol–gel spin-coating method. Surface morphology, optical and electrical properties of ZnO films at various sintering temperatures was investigated. The SEM images show the thin films prepared using 1.0 M solution is dense. The crystalline size as measured by Scherer's formula show increment with sintering temperatures. The optical transmittance result shows no specific pattern with sintering temperatures mainly due to the thin films defect. The optical absorbance of ZnO thin film at the UV region improved at higher sintering temperature. I-V measurement results suggested the improvement of ZnO thin film conductivity with sintering temperatures.

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