STUDY ON ELECTRICAL PROPERTIES OF ZINC OXIDE THIN FILMS PREPARED BY SOL GEL SPIN COATING

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Abstract - This project focuses on the effect of annealing temperature to electrical, structural and optical properties of deposited Zinc oxide (ZnO) thin films. ZnO solutions are deposited onto glass and silicon substrates using sol-gel spin coating technique. Deposited films are annealed at various temperatures from 300°C to 500°C. The electrical properties are characterized using Current-Voltage (I-V) measurement. I-V characterization result shows that resistivity decreased when annealing temperature increased. The structural properties are characterized using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). From SEM analysis it is observed that surface morphology becomes denser when temperature increases. The XRD indicate the crystallinity is better at higher temperature. UV-visible (UV-vis) spectrophotometer indicates transmittances are over 40% in visible region and the absorption edges are clearly observed at every sample.

Keywords: Zinc Oxide (ZnO); sol gel; thin film; spin coating; IV measurement.

I. INTRODUCTION

ZnO is an n-type semiconductor with direct band gap energy of 3.37 eV at room temperature and a free-exciton binding energy of 60 meV [1]. The property of ZnO is dependent partly on the crystallinity, crystallographic orientation, crystallite size and morphology.

Interest in the research effort on ZnO is driven by various applications in blue and ultraviolet (UV) light emitters [4, 3], solar cell windows [8, 9], photovoltaic device, gas sensor and surface acoustic wave device [13]. ZnO is well known for its transparency when made into thin films and is expected to find wide use as transparent electrodes for many devices, such as electrochromic displays, electroluminescent displays, and liquid crystal displays (LCDs) and solar cells.

ZnO thin films have been prepared by a variuos of techniques, such as R.F. magnetron sputtering [14, 5], reactive magnetron sputtering, chemical vapor deposition [7, 10], ion-beam evaporation, electron-beam evaporation, spray pyrolysis [6, 11], laser ablation and sol-gel process [12, 2].

Among the different techniques available, the sol-gel method seems to be the most attractive due to easy of coating on the desired shape and area, easy control of the doping level, solution concentration and homogeneity without using expensive and complicated equipment when compared to other methods.

Spin coating is used to apply uniform thin films to flat substrates. Generally 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. This technique is used in various applications that need to yield flat substrates that are coated with thin layers of material. Properties of films are affected by several factors such as effect of annealing temperature [15], annealing time, annealing ambient [8], and type of substrate [9]. Therefore it is very important to study the dependence of structural, morphology, electrical and optical properties on the annealing temperature and annealing time of ZnO thin film.

In this project the affect of annealing temperature on the electrical, structural and optical properties are investigated. This project involved depositing ZnO solution onto glass and silicon substrate using sol-gel spin coating technique. The material used Zinc acetate dehydrate (ZnAC) as starting material, 2-Methoxyethanol as solvent and monoethanolmine (MEA) as stabilizer. The surface morphology, structural, electrical and optical characteristic are characterized using SEM, XRD, I-V measurement, and UV-Vis respectively.

II. METHODOLOGY

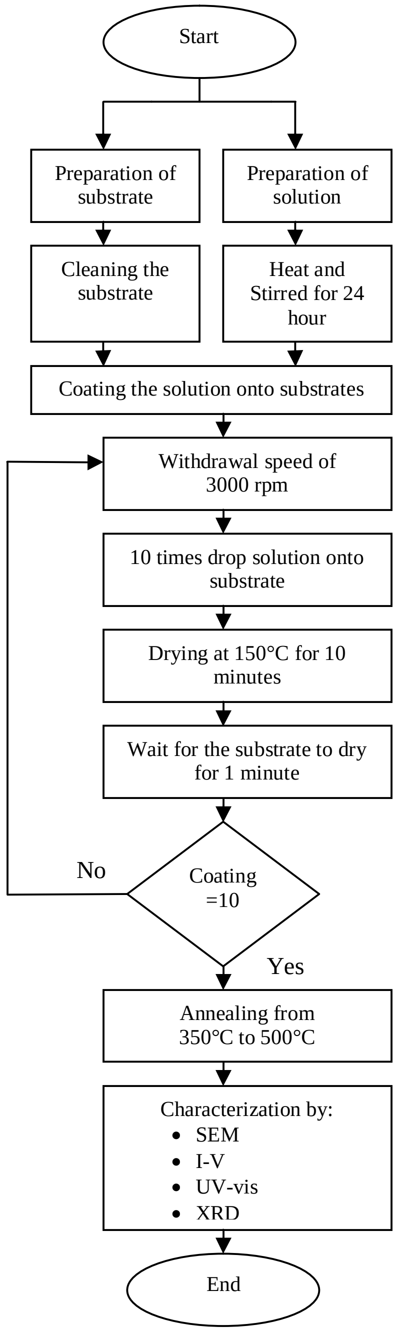

Figure 1: Flow chart of ZnO thin film preparation

Figure 1 shows the flow chart of ZnO thin films preparation. The flow chart indicates general flow of conducted experiment. In solution preparation stage, ZnAC (starting material) is dissolved in 2-Methoxyethanol (solvent) and monoethanolmine (MEA) (stabilizer) with molar ratio of ZnAC to MEA is 1:1. Solvent are added to dissolved reactants and reagents and provide temperature control, either to increase energy of the colliding particles or to absorb heat that is generated during an exothermic reaction. Stabilizer is used to prevent colloids from aggregating and increase the conductivity of the film.

The solution are then stirred and heated at 80°C for 3 hours to increase reaction process between materials in the solution. Then it is stirred at room temperature for 24 hours to reinforce gel network and yield clear solution.

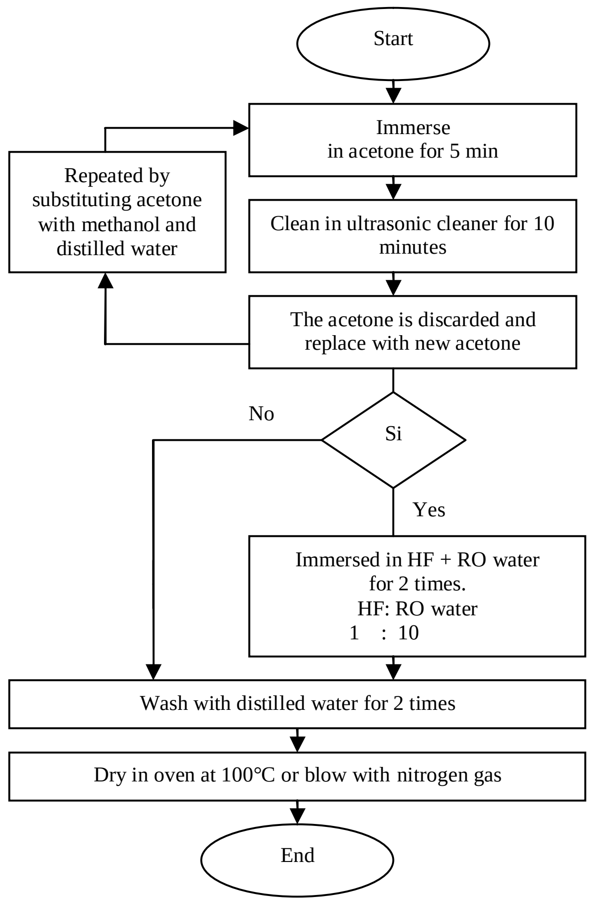

Figure 2: Flow chart of substrate cleaning process

Figure 2 shows the flow chart of substrate cleaning technique. Different substrate may have different cleaning technique so it is important to use a right cleaning technique to ensure the substrate is free from contamination. The process of cleaning for glass and silicon substrate is almost similar. The substrates are cleaned with acetone for 5 minutes and using vibration by sonification method for 10 minutes. Then the acetone is discarded and replace by new acetone and clean again for 5 minutes. This step is repeated by replacing acetone with methanol and distilled water. The silicon substrate is etched with hydrogen fluoride for 2 times and clean by using distilled water for 2 times. Then it is blow with nitrogen gas or dried in oven. The glass substrate does not have to be etched, it proceed to the drying process.

At deposition process, ZnO films are deposited on the substrate using spin coating technique. The solutions are dropped onto substrate while spanned at 3000 rpm for 60 second. The substrates then undergo heated process where it is heated at 150°C for 10 minutes to evaporate the solvent and to eliminate the organic component in the film. This drop and dry process is repeated for 10 times to yield required thickness. The deposited film is annealed in furnace at 350°C, 400°C, 450°C and 500°C. It is annealed at various different temperature to allow the study on it effect to the electrical, structural and optical properties.

In characterization process, films are characterized according to electrical structural and optical properties. The electrical and optical properties are characterized using I-V measurement and UV-Vis respectively. The optical absorption studies are carried out within wavelength range 200 to 800nm. The structural properties are determined by using SEM and XRD. Surface morphology is determined by SEM while crystalline structure is observed by XRD.

III. RESULTS AND DISCUSSIONS

A. Electrical properties of ZnO thin film

ZnO thin film was deposited onto glass substrate to measure it resistivity. Pt was deposited to the substrate to act as electrode. This electrode can reduce the series resistance without significantly interfere with the incoming light. The structure of the ZnO thin films on the glass substrate is as shown in figure 3. Two probes were tabbed on the coated platinum area to measure it electrical properties.

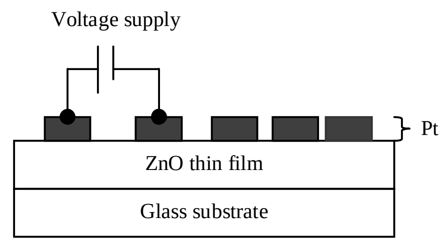

Figure 3: Structure of ZnO thin film deposited on glass substrate

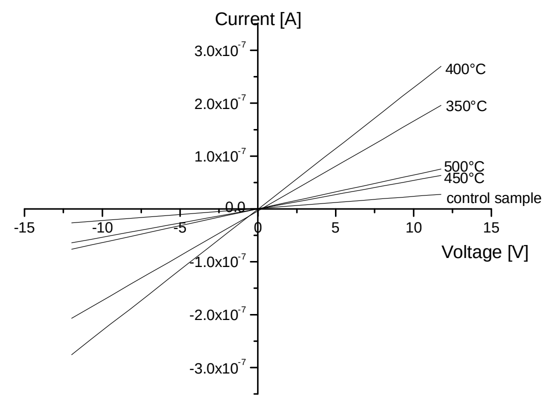

Figure 4: I-V characteristic of ZnO thin film

Figure 4 shows the I-V characteristic of ZnO thin films. The linear dependence indicates an ohmic behavior of the platinum contact in all the films. I-V curve shows that it is in forward bias. It means that the negative potential was applied to the n-type substrate whereas positive potential to the p-type substrate. When voltage is applied, both electron and holes in the n-type and p-type material is pushed toward the junction. The holes recombine with electron at the junction hence increase the number of negative ion. This will leave the n-junction with less number of positive ions.

Hence decrease the number of positive and negative ion at p-n junction. It result the shrinking of the depletion region. As the applied voltage exceeds the internal electrical imbalance, current carriers of both types can cross the junction into the opposite ends of the crystal. The electrons in the p-type side attracted to the positive applied voltage, while holes in the n-type side are attracted to the negative applied voltage. This will generate a complete current path through the junction. The current will flow and increase accordingly to the magnitude of the voltage applied to the circuit (Refer to equation 1).

$$V = IR \quad (1)$$

V = voltage
I = current
R = resistance

Resistivity of ZnO thin films increase when the resistance increase (Refer to equation 2).

$$\rho = \frac{RA}{L} \quad (2)$$

A = film thickness x length of platinum
L= length between platinum and platinum
ρ = resistivity

Table 1: Resistance of Zno film with annealing temperature

Annealing temperature (°C)	Resistance (Ω)
350	6.15E7
400	4.39E7
450	1.85E8
500	2.81E7

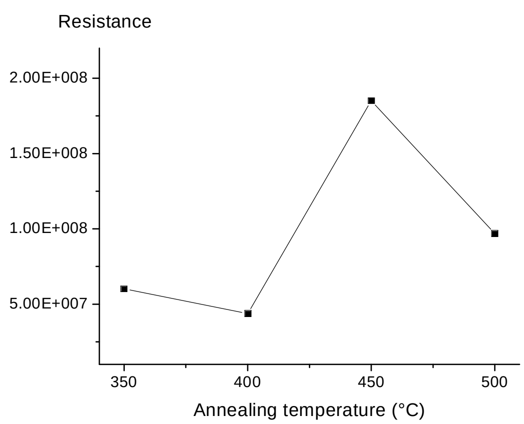

Figure 5: Plotted resistance of Zno film with annealing temperature

Table 1 shows the result of Zno film resistance with annealing temperature and figure 5 shows the plotted result. Figure 5 shows the resistance decreased as the annealing temperature increased except for the sample annealed at 450°C and 500°C. Further investigate showed those sample are defective and unreliable for investigation. Equation 2 shows relationship between resistance and resistivity. By assuming A and L in equation 2 are constant. Resistivity decreased as resistance decreased.

It can be concluded that resistivity of ZnO films decreased at higher annealing temperature. The reason that the resistivity increase (in 450°C and 500°C) with increasing temperature is that the number of imperfection in the atomic lattice structure increases with temperature and this hampers electron movement.

These imperfections include dislocation, vacancies, interstitial defects and impurity atoms. At above absolute zero, the lattice atoms are not always found in their lattice sites, it might participate and interfere with the directional electron movement. Thermal energy causes the atoms to vibrate about their equilibrium positions. At any moment in time many individual lattice atoms will be away from their perfect lattice sites and this interferes with electron movement.

$\rho = 1/\sigma$ ………… Equation 4

σ = conductivity
ρ = resistivity

$\rho = 1/q\mu N$………….. Equation 5

ρ = resistivity
q = charge (1.602 x 10-19)
μ = carrier mobility
N = carrier density

The conductivity of ZnO thin films also reflects the carrier mobility of the film. Which means when the conductivity increased the resistivity decreased (Refer to equation 4). Therefore carrier mobility of the film also increased when the resistivity decreased (Refer to equation 5).

B. *Structural properties of ZnO thin film*

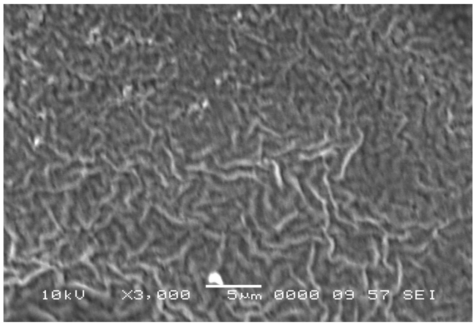

Figure 6: SEM image of ZnO thin films deposited on Si substrate annealed at 350 °C

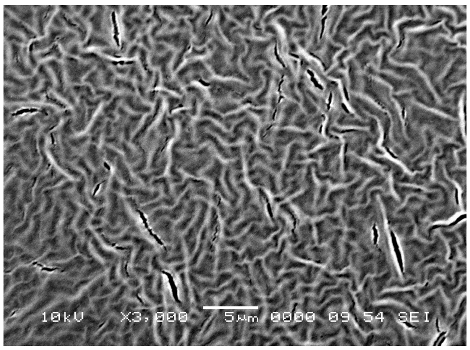

Figure 7: SEM image of ZnO thin films deposited on Si substrate annealed at 450 °C

The surface morphology of ZnO thin films has been characterized by SEM. Figure 6 and 7 show the surface morphologies of ZnO thin films on Si substrate annealed at 350°C and 450°C for 1 hour, respectively. The result shows that at higher annealing temperature the size of ZnO particles becomes bigger, the crystalline surface structure improved and grain boundary become denser and clearer.

The surface contact between ZnO particles depend to the denser of the film. The denser the film, the more surface contact exist between ZnO particles this result the improvement of the electrons mobility in the films thus provide better electrical properties.

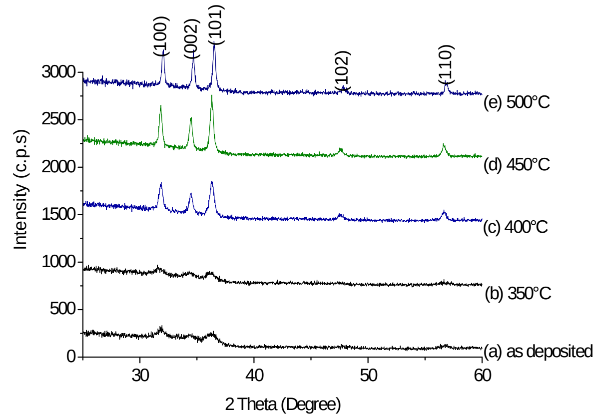

Figure 8: XRD spectra of ZnO thin films

Figure 8 shows XRD spectra for ZnO thin films deposited on Si substrate. The result shows that the ZnO thin film prepared exhibit polycrystalline structure with growth orientation at (100), (002), (101), (102) and (110). The annealed sample particles have a better crystallized compare to the sample without annealing (as deposited). This is showed by the comparison of the diffraction from the as deposited sample curve. The sharper peaks indicate the crystallinity of the films. The sharper peak at all peak at higher annealing temperature indicate improvement in crystallinity of ZnO thin film at higher annealing temperature. This can be interpreted from nucleation theory [12]. According to the theory, for a perfect hetero-epitaxy nucleation, the substrate temperature must be higher than the critical value during the deposition process, therefore, the crystallinity of the films in the experiment improved when the substrate temperatures increased from 350 to 500°C.

C. *Optical properties of ZnO thin film*

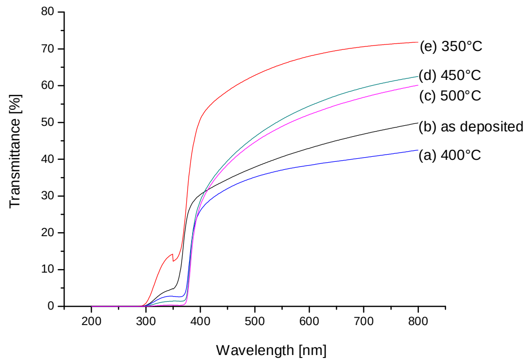

Figure 9: Optical transmittance spectra of ZnO thin films

Figure 9 shows the optical transmittance spectra in the length range 300 to 800 nm in ZnO films grown at various substrate temperatures. The films are highly transparent in the visible region with more than 40% transparency within 400 to 800 nm.

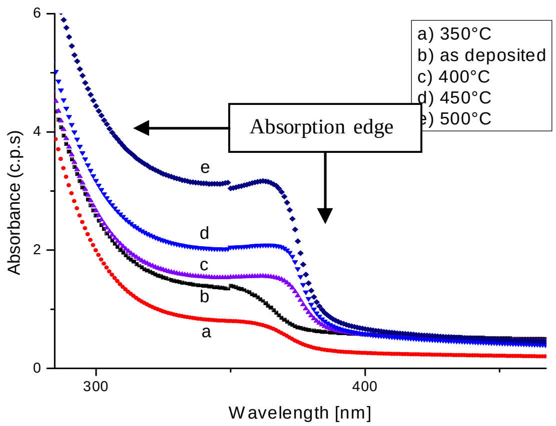

Figure 10: Optical absorption spectra of ZnO thin films

Figure 10 shows the optical absorption spectra of ZnO thin film. The width of the absorption edge of the self assembly film indicates that there exist defect-related transitions. Defects usually create discrete electronic states in the band gap, and therefore influence both optical absorption and emission processes. The two most common defects in ZnO are likely to be oxygen and zinc vacancies and the visible band in the absorption spectrum can be related to the presence of these defect states in the self assembled film.

IV. Conclusions

ZnO thin films are prepared on glass and silicon substrate by the sol–gel spin-coating method. Zinc acetate is used as a precursor, 2-methoxyethanol as a solvent, and MEA as a stabilizer. Electrical, structural and optical properties of the films at various annealing temperatures are investigated. I-V measurement study shows that when annealing temperature increased resistivity decreased. From SEM analysis it shows that surface morphology become denser at higher temperature. While XRD result shows that ZnO crystallinity improved at higher annealing temperature. The UV-Vis result shows that transmittance was over 40% in the visible region and fundamental absorption edges were clearly observed for entire sample.

V. Future Development

For future development, ZnO thin film can be fabricated using nanotechnology to create a nanoparticle size of ZnO thin films. Nanotechnology mainly consists of the processing of, separation, consolidation and deformation of materials by one atom or by one molecule. Manufactured products are made from atoms. The properties of those products depend on how those atoms are arranged. The diamonds can be produce if the atoms in coal can be rearranged. Silicon and computer chips can be produce if the atom in sand is rearranged. With this technology a very strong, inexpensive, and very light material such as car and diamond can be produce. It could also make almost every manufactured product faster, lighter, stronger, smarter, safer and cleaner. This technology has a very bright future and still developing.

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