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TO DEPOSIT ZnO THIN FILMS VIA ELECTRODEPOSITION AT DIFFERENT pH VALUES

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ABSTRACT

Thin films of zinc oxide (ZnO) were synthesized by using electrodeposition. The films were produced at three pH value of 6, 7 and 8. Effects of pH on film structure and morphology were investigated in detail. The peaks observed from patterns of X-ray diffraction (XRD) showed that all films formed in hexagonal crystal structure. The optical properties were determined by using absorbance measurements. The optical band gap increased from the 3,17 eV to 3,57 eV as the pH was reduced from the 8 to the 6. It is observed from the scanning electron microscope (SEM) that pH effected surface properties.

Keywords: ZnO; zinc oxide; electrodeposition; pH; thin film

1. Introduction

Zinc oxide (ZnO) is a unique metal oxide semiconductor with relatively wide band gap energy of 3.3 eV, a relatively large exciton binding energy of 59 meV and high electron mobility, thus making transparent n-type conductivity and room-temperature UV emission possible [1]. ZnO is widely used in a variety of industrial and technological applications such as surface acoustic wave devices, piezo-electric films, catalysis, chemical sensors and photovoltaic applications [2]. ZnO films have been prepared by several techniques such as spray pyrolysis, RF magnetron sputtering, chemical bath deposition, molecular beam epitaxy, chemical vapour deposition, and electrodeposition. Some groups reported nitrate ions or molecular oxygen as precursors for ZnO electrodeposition [3]. Electrodeposition is a low cost alternative for fabrication of ZnO thin film that offers the possibility of a high degree of control over the film characteristics through optimization of the deposition parameters [4].

The ZnO formation may be proposed by following equations [5].

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2$$

$$Zn(OH)_2 = ZnO + H_2O$$

The reaction between Zn and O may occur as the following equation:

$$Zn^{2+} + 0.5O_2 + 2e^- \rightarrow ZnO$$

It is presented in this study that effect of pH on ZnO thin films. It is observed that when pH was 6, the transmittance is relatively high. Thus, it can be said that this film may be suitable for solar cells.

2. Experimental Details

Chronoamperometry of electrodeposition was used to deposit ZnO films. A cell with three electrodes such as platinum wire, a saturated calomel reference electrode and indium tin oxide (ITO) were used in depositions. The electrolytes consisted of 0.01M $Zn(NO_3)_2$ and 0.1M KCl in 100mL. Depositions potential were chosen as to be -0.9 V and all depositions were completed in 20 minutes. The depositions temperature was hold at 70±2 °C with using a heater and stirrer. The solutions were stirred at 600 rpm. The pH of the solutions was chosen as to be 6, 7 and 8. The final solution pH without any additive was measured as to be 7 and (1)

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pH was increased with using NaOH to 8 and reduced by using dilute HCl acid to 6.

A JASCO V–530 with double beam uv spectrometer was employed to measure absorbance values versus wavelength. To analysis structures of the films a PANalytical empyrean X-ray diffractometer was used. The morphologic characterizations of the ZnO were investigated by a Zeiss supra 40VP SEM with 50000 times magnified.

3. Results and Discussion

3.1. XRD analysis of the ZnO films

The gravimetric method has been widely used to determine of the film thickness. Film thicknesses were calculated by gravimetric method in this study. The ZnO thicknesses were 274 nm, 253 nm and 218 nm according to the pH of electrolyte of 6, 7 and 8 respectively.

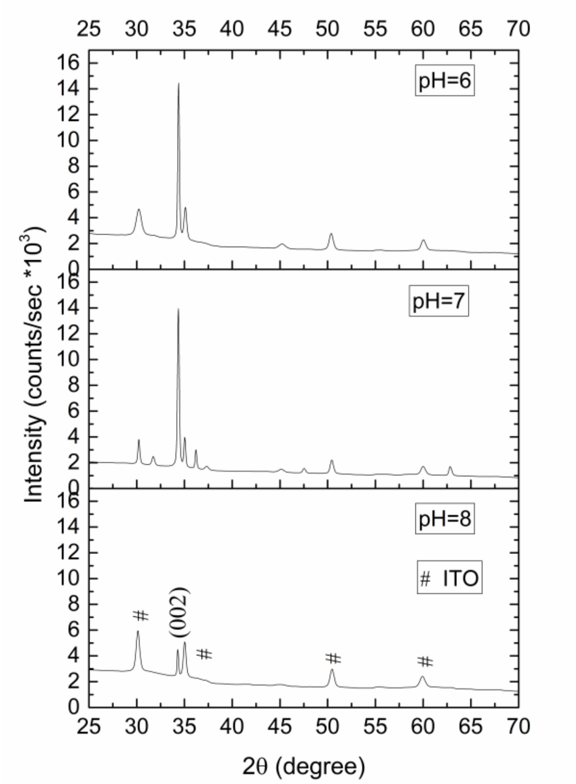

Figure 1. XRD patterns for ZnO thin film deposited by electrodeposition at different pH values

Fig. 1 shows the patterns of the XRD for ZnO thin films. The peaks indicate that there are the hexagonal forms of ZnO films. The peak intensity of the films obtained at pH 6 and 7 is relatively high although the all films have nearly same thicknesses. This indicates that there is good crystallization of these films.

In this study, Scherrer formula was used to calculate crystallite size. Sherrer equation is given in Eq. 5.

$$cs = \frac{K x \lambda}{B x \cos\theta} \quad (5)$$

where cs is the mean crystallite size, λ is the wavelength of X-ray radiation (1.54Å), K is the Sherrer constant, B is the full width half maximum of peak height and θ is the Bragg's angle [2]. The calculated crystallite sizes are 27, 38 and 46 according to the pH of 6, 7 and 8 respectively. It is concluded that when pH was reduced, the reaction rate decreased and thus crystallite size also decreased.

3.2. Optical analysis of the ZnO films

The absorbance values versus wavelength are given in Fig. 2. The sharp increases were observed at wavelength of 350 and 400 nm. The sharp increase shifted from the 400 nm to the 350 nm as the pH was reduced from the 8 to the 6.

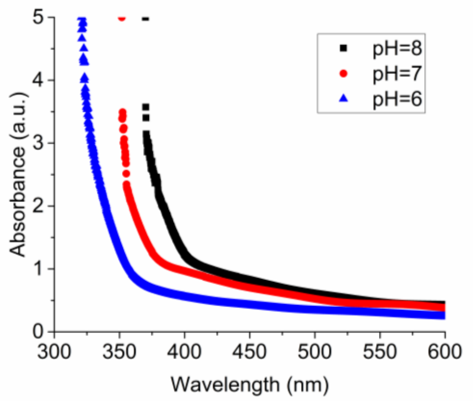

Figure 2. Optical absorptions of electrodeposited ZnO films of various pH values

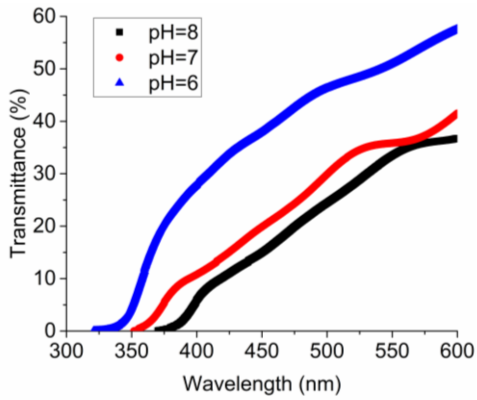

Figure 3. Optical transmittance of electrodeposited ZnO films of various pH values

The transmittance values were calculated by using absorbance measurements and these values were given in Fig. 3. The transmittance of the film obtained at pH of 6 is relatively high. There may be a variety reasons such as low thickness, good crystallization and low surface roughness.

In order to determine optical band gap of thin film material, Tauc plot is used. The absorption coefficient and photon energy are related by the following equation:

$$(\alpha h\nu)^m = A(h\nu - E_g)$$

In the above equation, Eg is the band gap of the material, A is a constant, and m has different values depending on the optical absorption process [6]. The straight-line portion of the curve, as extrapolated to zero, causes to estimating of the band gap energy. In order to estimate energy band gap, plots of $(\alpha h\nu)^2$ versus hν are given in Fig. 4 for the ZnO films. The energy band gaps varied between 3,17 and 3,57 eV. The energy band gaps decreased as pH of the solutions was increased. It is concluded that reaction rate effected crystallite sizes and thus energy band gap.

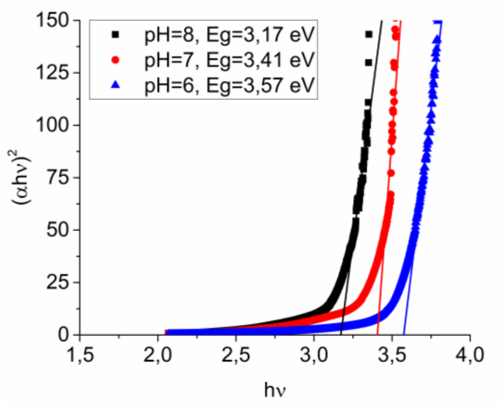

Figure 4. For the ZnO films plots of $(\alpha h\upsilon)^2$ vs. hυ

3.3. Surface studies of ZnO thin films

50000 times magnified surface images of the ZnO films were obtained by using a SEM and these images were given in Fig. 5. There are nanorods on the all surface. The diameters of the rods on the surface of the films obtained at pH 7 and 8 varied between 100 and 400 nm. Besides all rods covered surface of these ZnO films. On the other hand, the rods of the surface of the film obtained at pH 6 were scarcely and diameters of these rods nearly 200 nm and homogenous. There are no voids, cracks or pinhole on the surface of all films.

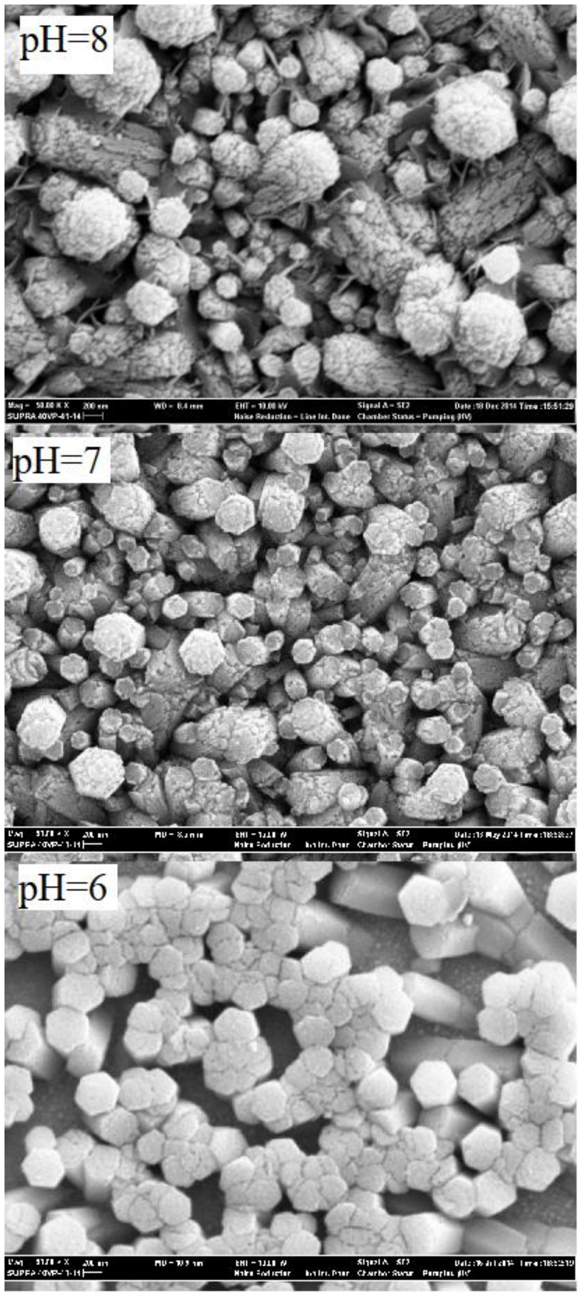

Figure 5. 50000 times magnified top view SEM images of thin films of ZnO

Conclusion

In this work, polycrystalline ZnO films were precipitated onto ITO coated glass substrates. The depositions were carried out a potentiostad /galvanostad with using chronoamperometry of electrodeposition at pH value of 6, 7 and 8. The pH effects were researched in detail. It is understood according to the film thicknesses that pH effected reaction rate. The reaction rate decreased as the pH of the final electrolyte was reduced. The decrease of the reaction rate caused the decreasing crystallite size. The energy band gap of the films increased from the 3,17 eV to the 3,57 eV due to the decreasing crystallite size. The surfaces were analyzed with using SEM images. SEM images showed that there are no cracks, pinhole and voids on the surfaces. Besides, surfaces were covered nanorods.

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