

Influence of deposition potential on ZnO films obtained by electrodeposition

^{1*}Ayça Kıyak Yıldırım, Barış Altıokka²

^{1*}Bilecik Vocational School of Higher Education, Bilecik Şeyh Edebali University, Bilecik 11210 Turkey
²Bilecik Vocational School of Higher Education, Bilecik Şeyh Edebali University, Bilecik 11210 Turkey

Abstract :

Thin films of ZnO electrodeposited on ITO coated glass substrate at different potential ranging from -0,8 to -1,1 V. In the experiments ZnCl2 was used as an electrolyte and depositions temperature were keept at 75°C during the depositions. Structural analyses were carried out by XRD and XRD results revealed that all films formed hexagonal crystal structure. The optical properties of the films were researched by using UV-vis spectrophotometer. The energy band gaps of the ZnO films are between 3.51 and 3.80 eV. The morphological analyses were performed by SEM with coating platinium. It was understand from the SEM images that various morphological structure was obtained such as slice, lamellar and lace like structure.

Key words: ZnO, deposition potential, Energy Band Gap

1. Introduction

The figure out the synthesis of semiconductor crystals with precise structures shapes and sizes has appeal to strong enthusiasm in consideration of comprehend their unique properties which are not only count on their structure, phase, size, size distribution and shape, but also chemical composition [1]. ZnO is one of the most attractive oxide semiconductor crystal for nanotechnology due to its wide band gap (3,4 eV) and its large exciton binding energy (60 meV) for the potential applications [1,2]. However, among various synthesis methods the electrodeposition represents an interesting approach for producing of ZnO films and attracted more attention due to its major advantages namely low cost and scalability [3]. The producing of a variety of ZnO films such as one dimensional nanowires/nanorods nanoribbons, nanotubes and two dimensional nano-structures have been sufficiently research in recent years. [4,5]. It is well known that hierarchical nanostructures have considerable attention during to their promising applications to nanodevices such as light-emitting diodes, field-effect transistors, chemical sensors, solar cells, sensors, photovoltaic cells, and nanogenerators [1,2]. ZnO films growth was controlled by electrodeposition parameters such as electrolyte bath composition, pH, deposition potential or deposition current density and temperature [1]. Consequently, we focused our research on the way in which ZnO films optical properties and morphology is obtained from ZnCl₂ solutions are influenced by the value of the deposition potential.

2. Materials and Method

In this work, ZnO films were produced by electrodeposition approach using in the electrodeposition bath is based on $0,05 \text{ M ZnCl}_2$ aqueous solutions. Additionally, the deposition solution contains 0,1 M KCl as a supporting electrode. The pH value of aqueous solution is

*Corresponding author: Address: Faculty of Engineering, Department of Civil Engineering Sakarya University, 54187, Sakarya TURKEY. E-mail address: caglar@sakarya.edu.tr, Phone: +902642955752

regulated to be 5,86 utilized a pH meter. Quantity of aqueous solutions is hold on the physically at $75\pm2^{\circ}$ C temperature along the deposition.

The electrodeposition process was carried out in IVIUM VERTEX Potentiostat/Galvanostat system that is a conventional three electrode electrochemical cell set-up. ITO coated glass as working electrode employed are a platinum wire is used as counter electrode which has approximately1 cm² surface The reference electrode was a commercial Ag/AgCl saturated calomel electrode. ITO coated glass substrates having deposition area of 1,65 cm² and sheet resistance of 25 Ω /cm. Before the electro deposition, ITO coated glass substrates were bathe with acetone and afterwards they stir in the deionized water and given up for drying under environmental condition.

Electrodepositions were achieved potentiostatically. A Potentiostat/Galvanostat was employed for controlling the different cathodic potentials which is called deposition potential intermediate to -0,80 V and -1,10 V with mixing up 600 rpm at (versus Ag/AgCl) seeing 30 minute deposition time.

After electrodeposition the samples were extensively characterized by means of using JASCO V-530 UV-vis spectrophotometer, using PANalytical Empyrean XRD and using Zeiss SURA 40 VP SEM. To be understood to optical properties of the films, we used absorbance measurements which were made at wavelength between 300nm and 600nm. To be obtained the structural analyses of the films we were interpreted XRD results. Lastly, the morphological properties of the films were explicated by SEM results.

3. Results and Discussion

3.1. Optical Properties of the ZnO Films

The absorbance measurements towards wavelength of the films generated are demonstrated in Fig. 1. The absorbance of the films which was come by the -1,10 V cathodic potential shifted high wave length values like as 370 nm. The band gap of the films were obtained by the $(\alpha hv)^2$ versus hv graphs which are indicated in Fig.2. The band gaps of the films which is acquired at -0,80 V; -0,90 and -1,0 V cathodic potentials were approximately same value as 3,80 eV. These value is relatively high than the values of the literature. Adversely, the band gap of the film obtained at -1,10 V cathodic potential is 3,51 eV. This value not only high than the values of the literature, but also is lower than the other films which is obtained at 0,80 V; -0,90 and -1,0 V cathodic potential.

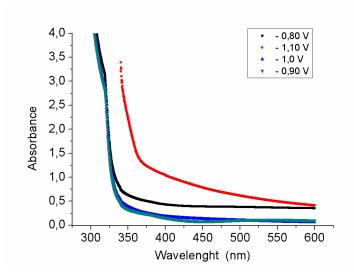


Figure 1 Absorbance versus wavelength graphs

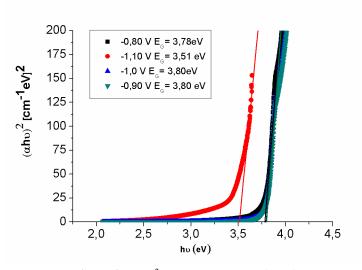


Figure 2 $(\alpha h v)^2$ versus hv graphs of the films

3.2 X ray diffraction analysis

The XRD patterns of the obtained ZnO films are demonstrated in Figure 3. It is shown from the Fig. 1 that all films have strong (002) peak intensities. This peak related to the hexagonal structure.

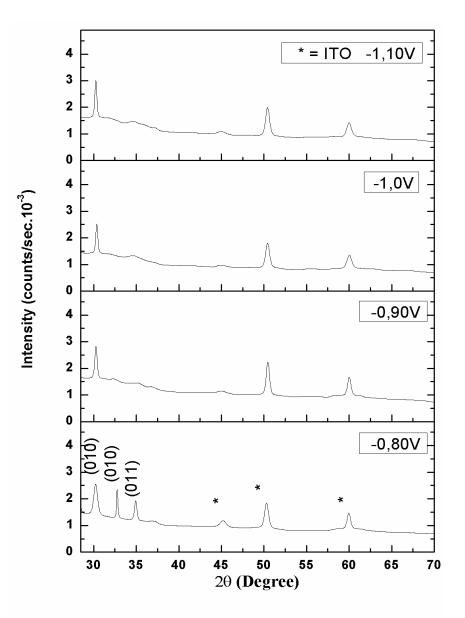


Figure 3 XRD patterns of the ZnO films

The peak intensities of the films obtained at pH 6 and 7 are relatively high. It is concluded that this situation related to the film thickness and good crystallization.

Debye Scherrer equation which is given in Eq. 1 were used to calculated the crystallite sizes of the films

$$cs(crystallitr size) = \frac{0,089 \cdot 180 \cdot \lambda}{3,14 \cdot B \cdot \cos\theta} (nm)$$
(1)

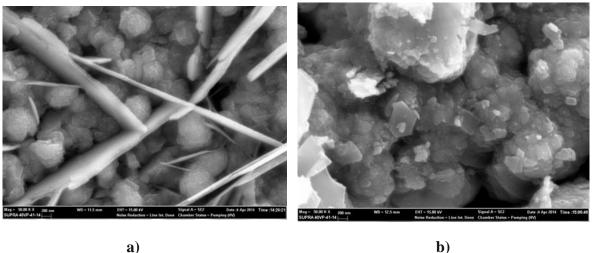
where λ is the wavelength of X-ray radiation (1.54056 Å), 20 is the position of peak center, B is the full width at the half maximum of peak height (in degrees) [6]. The results of crystallite sizes

of the films are given in Table 1. It is clearly indicated from the Table 1 that among the crystallite size of the films which is produced at -0,80 V are relatively lower than the other films. Gravimetric method was used to calculate of the film thickness, and The results of film thickness were given by Table 1. The thickness of the film which are produced at -0,90 V and -1,0 V are relatively lower than that of the other films.

Table 1 Calculated crystallite sizes and film thicknesses of the ZnO films					
Deposition	-0,80 V	-0,90 V	-1,0 V	-1,10 V	
Potentials					
Crystallite size(nm)	35	56	33	67	
Film thickness (nm)	432	653	684	598	

3.3 Surface Morphologies of the Films

The 50000 times intensified SEM images of the films are shown in Fig. 4 respectively for different cathodical potential. When Fig. 4a was examined, it is clearly shown that the surfaces were covered slice like ZnO crystals. Under this slice like structure there are lamellar like structures were existed. The surface of the films obtained at -1,10 V cathodic potential shown in Fig. 4d was slice like ZnO crystals which was bigger than as the Fig. 4a . It is also shown Fig. 4a under this slice like ZnO crystals ssurfaces were covered broken pieces of ZnO. It is clearly demonstrated in Fig. 4b the surface covered rod which was bring together lamellar ZnO crystals, but end of the rods is degenerated and not same form. The most different surface structure was seen in Fig. 4c, it is covered lace like ZnO crystals.



a)

Figure 4 50000 times magnified SEM images of the films obtained at deposition potential a) -0,80 V, b)-0,90 V

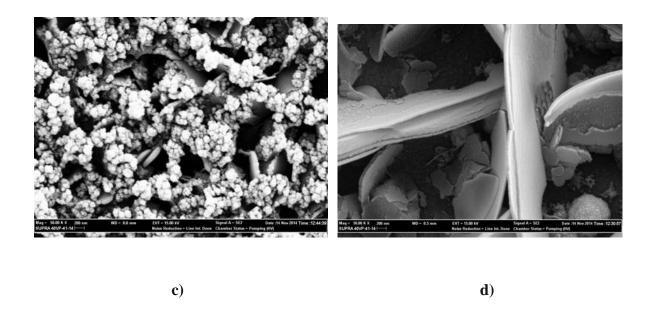


Figure 4 50000 times magnified SEM images of the films obtained at deposition potential c) -1,0 V, d)-1,10 V

Conclusions

In this study, ZnO films were fabricated by different deposition potentials.. In the literature, band gap of the ZnO films is average 3,40 eV however the films which is acquired at -0,80 V; -0,90 and -1,0 V cathodic potentials having approximately same value as 3,80 eV. Because of these results the films may be suitable for gas sensors.

Reference

- [1] Azizi, A., Khelladi, M., Mentar, L., Subramaniam, V. (2013), "A study on electrodeposited of Zinc Oxide nanostructures," *Journel of Materials Science Materials in Electronics*," 24(1), 153-159
- [2] Dai Shuxi, Li Yinyong, Du Zuliang, Carter Kenneth R., Electrochemical deposition of ZnO hierarchical nanostructures from hydrogel coated electrodes, Journal of The Electrochemical Society, 2013 160(4): D156-D162
- [3]Enculescu, I., ve Matei, E. (2011), "Electrodeposited ZnO films with high UV emission properties," *Materials Research Bulletin*, **46**, 2147-2154
- [4]S. Xu, Z. L. Wang, Nano Research 2011, 4, 1013-1098
- [5] M. Ahmad, J. Zhu, J. Mater. Chem. 2011, 21, 599-614
- [6] Bhowmik R.N., Nrisimha Murty M., Sekhar Srinadhu E., Magnetic modulation in mechanical alloyed Cr1.4Fe0.6O3 oxide, PMC Physics B 2008, doi:10.1186/1754-0429-1-20