

Effect of Potential on Structural, Morphological and Optical Properties of ZnO Thin Films Obtained by Electrodeposition

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Abstract: Polycrystal ZnO thin films have been deposited on ITO coated glass substrate in two different potential of -0.85 V and -0.95 V by electrochemical deposition technique using 0.005 M ZnCl₂ or 0.01 M (Zn(NO₃)₂·6H₂O) at 72 ± 2 °C and with supporting electrolyte 0.1 M KCl aqueous solutions. Before the depositions, the solutions were saturated with oxygen by passing oxygen through the growth cell. The energy band gaps of the obtained films were estimated from the absorbance measurements. The energy band gaps of the films obtained using Zn(NO₃)₂ were between 3.49 and 3.57 eV while that of obtained using ZnCl₂ were between 3.60 and 3.63 eV. XRD (X-ray diffraction) results showed that all the films have a hexagonal structure. It was obtained by XRD that the crystallite sizes of the films are between 46 and 54 nm. Morphological characterization of the ZnO thin films was characterized from the SEM (Scanning electron microscopy) images. It is seen from the SEM images that the surface of the films are leafy and flaky form.

Key words: ZnO, electrochemical deposition, different potential, SEM (Scanning electron microscopy).

1. Introduction

Over the last few years, ZnO films have been growing and investigated because of their good optical and electrical characteristics and their transparency in the visible wavelength [1].

ZnO exhibit n-type feature [2] and its optical band gap vary from 3.2 to 3.4 eV at room temperature [3]. ZnO is direct band gap and it has relatively large exciton binding energy of 60 mV [4]. Zinc oxide exists in three forms as to be cubic zinblend, hexagonal wurtzite and rarely in cubic rocksalt structures. The most common structure is wurtzite and the zinblend form which can be stabilized by growing ZnO on substrates with cubic lattice structure. The rocksalt structure only form at high pressure of nearly 10 GPa [5].

A variety of techniques are used to deposit ZnO thin films such as metal organic chemical vapour deposition [6] RF magnetron sputtering [7, 8], pulsed

laser deposition [9], molecular beam epitaxy [10] spray pyrolysis [11], sol-gel [12] and electrodeposition with using aqueous solutions [13-16]. Among these techniques, the electrodeposition method has many advantages that is less onerous and widely used in industry. It is a low-temperature processing usually most of the deposits were carried under a temperature below 100 °C, which allows various substrate shapes and a controllable film thickness [1]. In addition to them, the morphology of the grown oxide varied much in grains size and shape from single nanobelts, nanowires [17], nanocolumns [18] and nanorods [19].

There are two ways to electrodeposit ZnO films such as cyclic voltamperometry which is an useful for analytical purposes and potentiostatic technique (chronoamperometry) for ZnO films elaboration.

2. Experimental Details

Polycrystal ZnO thin films were produced by electrodeposition from aqueous solutions composed of 5 × 10⁻² M ZnCl₂ with supporting electrolyte 0.1 M KCl or 1 × 10⁻² M Zn(NO₃)₂·6H₂O and with supporting

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electrolyte 0.1 M KCl. Before the film deposition, the ITO substrates and deposition cell were washed acetone and then rinsed with deionized water. The rinsed deposition cell and the ITO substrates were left to dry at room conditions. The final solutions temperature was held at 72 ± 2 °C. Before the depositions aqueous solutions were saturated with oxygen by passing oxygen through the growth cell for 40 min. IVIUM VERTEX Potentiostat/Galvanostat system with conventional three electrode cell was used for film deposition with ITO glass substrate having a sheet resistance of 25 Ω /cm as the working electrode with an effective deposition area of 1.65 cm². A platinum sheet was used as the counter electrode and an Ag/AgCl saturated electrode was used as the reference electrode to electrodeposition of ZnO thin films. Electrodepositions were carried out potentiostatically without stirring at different cathodic potentials -0.85 V and -0.95 V (versus Ag/AgCl) for 30 min in order.

The pH of aqueous solutions measured to be 6.29. Optical absorption spectrums of the obtained ZnO thin films were obtained between 300 nm and 600 nm range by JASCO V-530 UV-Vis double beam spectrometer. Surface morphology of ZnO thin films and Zn/O ratios was investigated by the scanning electron microscope ZEISS SUPRA 40 VP with coated platinum. XRD (X-ray diffraction) patterns of the films were recorded with a PANALYTICAL EMPYREAN high temperature X-ray diffractometer using Cu K α radiation (λ K α = 1.5418 Å) and the diffraction patterns of the ZnO thin films were recorded as a function of 2 θ angle.

3. Results and Discussion

3.1 Structural Properties of ZnO Films

Fig. 1 shows the XRD patterns of the electrodeposited ZnO thin films. It is seen from the Fig. 1 that all of the ZnO film have strong (002) preferred orientation. It is also seen from the Fig. 1 that the (002) peak intensity of the ZnO thin films obtained with using ZnCl₂ are higher than obtained with using

Zn(NO₃)₂·6H₂O at -0.85 V. Moreover, the ratio of the (002) peak intensity to the (011) peak intensity of the ZnO thin films which were obtained -0.85 V zinc nitrate, -0.95 V zinc nitrate, -0.85 V zinc chloride and -0.95 V zinc chloride are 3.33, 23.04, 13.28, 67.85, respectively. Moreover, XRD results showed that all of the films have a hexagonal structure.

The crystallite sizes of the ZnO films were calculated by measuring the full-width at half-maximum of the (002) peak using the following Scherrer formula:

$$cs = \frac{K\lambda}{B\cos\theta} \quad (1)$$

Where, *cs* is the crystallite size, *K* is the constant, λ is the wavelength of X-ray radiation (1.54 Å), *B* is the full width at the half maximum of peak height and θ is the Bragg's angle [20]. The calculated crystallite sizes are given in Table 1. The crystallite sizes were found to be

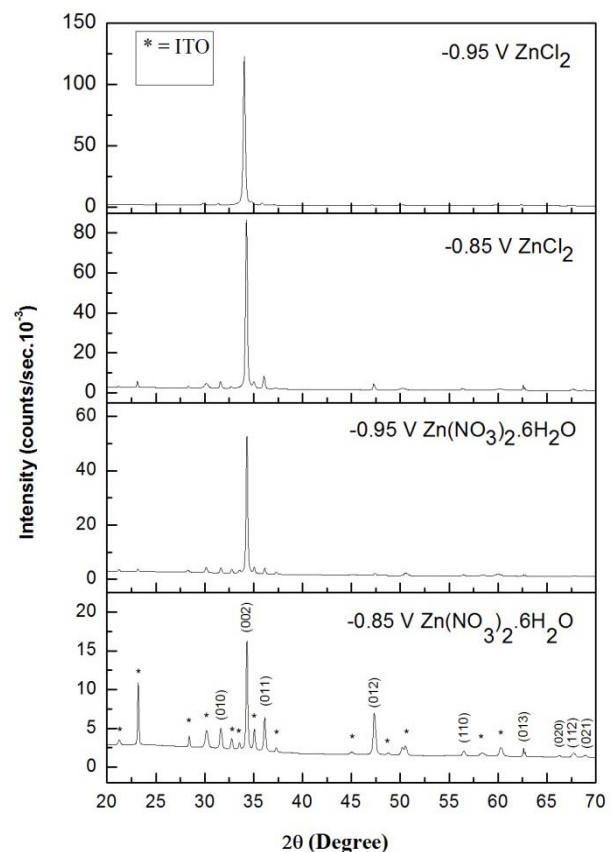


Fig. 1 The XRD patterns of the ZnO films that obtained in zinc nitrate at -0.85 V and at -0.95 V, in zinc chloride at -0.85 V and at -0.95 V.

between 46 and 54 nm. The crystallite sizes of the ZnO

films obtained using $Zn(NO_3)_2 \cdot 6H_2O$ have bigger than the obtained using $ZnCl_2$.

The thicknesses of the obtained films were calculated applying following Faraday's law:

$$t = \frac{1}{nFA} \left(\frac{QM}{\rho} \right) \quad (2)$$

Where, n is the number of electrons transferred, F is Faraday's number, A is the electrode area, Q is the accumulated charge during the electrodeposition, M is the formula weight (81.4 g/mol) and ρ is the density (5.6 g/cm³) [21]. The calculated film thicknesses are given in Table 2. With regard to the film thicknesses, the ZnO films obtained using $Zn(NO_3)_2 \cdot 6H_2O$ at -0.95 V have thicker than the obtained using $ZnCl_2$ at -0.95 V.

3.2 Optical Properties of ZnO Films

The absorbance spectra of the ZnO films are shown in Fig. 2. It was seen from the Fig. 2 that the ZnO films obtained in using $Zn(NO_3)_2 \cdot 6H_2O$ at -0.85 V and at -0.95 V have a high absorbance while the obtained in using $ZnCl_2$ at -0.85 V and at -0.95 V have low absorbance.

The transmittances versus wavelength plot are shown in Fig. 3. It was attracted attention in the Fig. 3 that the films obtained with Zink chloride demonstrate average 20% transmittance while the films obtained with Zink nitrate demonstrate average 7% transmittance at the 500 nm of wavelength.

For the thin film materials, a Tauc plot is used to

estimate the optical energy band gap. The Tauc theory is expressed by Eq. 3 [22]:

$$(ahv)^{1/m} = A(hv - E_g) \quad (3)$$

Where, A is a constant, E_g is the energy band gap and m is 1/2 and 3/2, for an allowed direct energy gap and a forbidden direct energy gap, respectively [22]. For the ZnO films, m is 1/2. E_g was estimated from the $(ahv)^2$ vs (hv) plot, which is given in Fig. 4. The energy band gaps of ZnO films varied between 3.49 and 3.63 eV. The energy band gaps of ZnO films obtained using zinc chloride are more than the energy band gaps of the films obtained using zinc nitrate.

The reflectance of the films are shown in Fig. 5. It is shown in Fig. 5 that the reflectance of the films obtained using zinc chloride demonstrate about half of the reflectance of the films obtained using zinc nitrate.

3.3 Surface Morphology of ZnO Thin Films

Fig. 5 shows the surface morphologies of ZnO films prepared at different cathodic potentials. The surface of the ZnO films prepared using zinc nitrate at -0.85 V (Fig. 6a) has more flakes than that of using zinc chloride at -0.85 V (Fig. 6b). Also, the ZnO films prepared using zinc chloride at -0.85 V formed leafy morphology. The flakes on the surface of the ZnO film prepared using zinc nitrate at -0.95 V (Fig. 6c) are quite increased and almost covered with the entire surface of the ZnO film. The flakes on the surface of the ZnO film

Table 1 The calculated crystallite sizes of the ZnO thin films.

Aqueous solutions compose	Supporting electrolyte	Cathodic potentials (V)	FWHM	Intensity	2θ	Crystallite size (nm)
1×10^{-2} M $Zn(NO_3)_2 \cdot 6H_2O$	0.1 M KCl	-0.85	0.1535	11,646.21	34.2867	53.5
		-0.95	0.1535	41,946.69	34.2855	53.5
5×10^{-2} M $ZnCl_2$		-0.85	0.1791	66,113.07	34.2387	45.9
		-0.95	0.1791	92,253.67	34.0155	45.9

Table 2 The calculated film thicknesses of the ZnO thin films.

Aqueous solutions compose	Supporting electrolyte	Cathodic potentials (V)	Deposition time (s)	Current (mA)	Film thicknesses (nm)
1×10^{-2} M $Zn(NO_3)_2 \cdot 6H_2O$	0.1 M KCl	-0.85	1,800	-2.104	1,806
		-0.95	1,800	-4.431	3,803
5×10^{-2} M $ZnCl_2$		-0.85	1,800	-2.321	1,991
		-0.95	1,800	-2.164	1,858

Effect of Potential on Structural, Morphological and Optical Properties of ZnO Thin Films Obtained by Electrodeposition

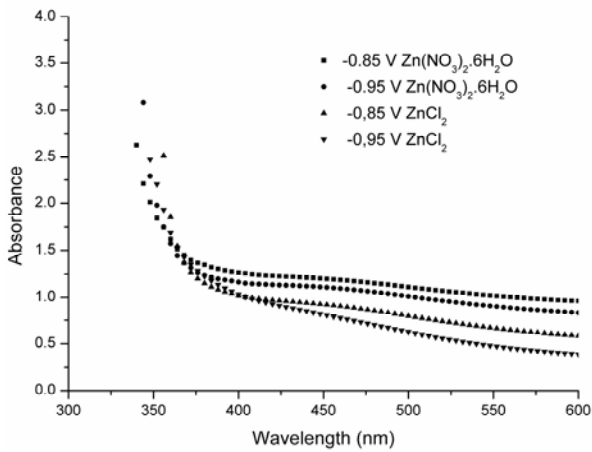


Fig. 2 Optical absorption spectra of the ZnO films obtained in zinc nitrate at -0.85 V and at -0.95 V, in zinc chloride at -0.85 V and at -0.95 V, the wavelength range from 300 to 600 nm.

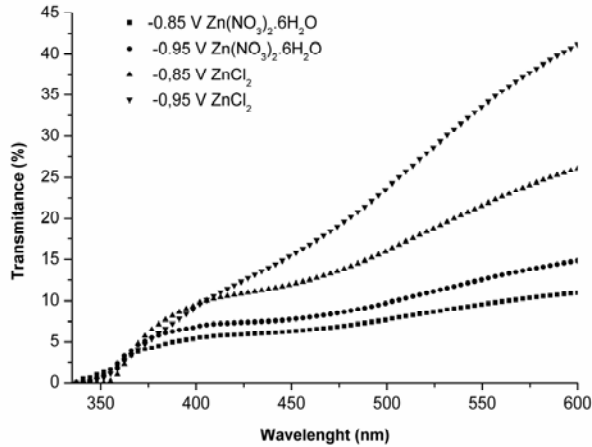


Fig. 3 Transmittances vs. wavelength plot of the obtained films.

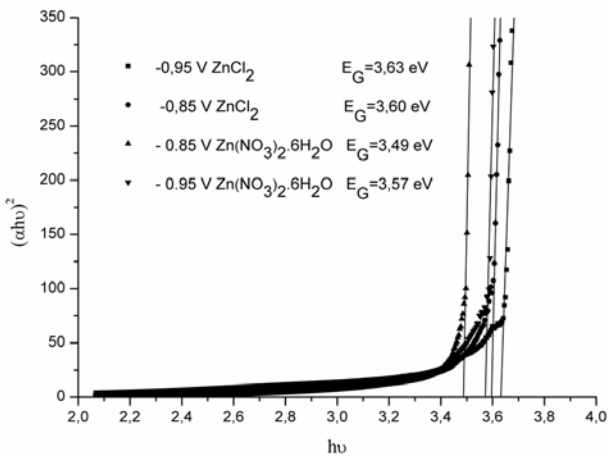


Fig. 4 Plots of $(\alpha hv)^2$ vs (hv) for the ZnO films.

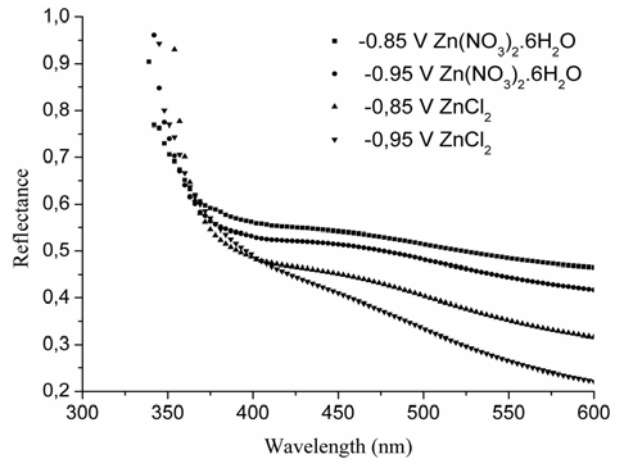


Fig. 5 Plots of reflectance versus wavelength.

prepared using zinc chloride at -0.95 V almost disappeared and the entire surface of the ZnO film is full of leafy nanoforms with diameters about 202 nm as is seen in Fig. 6d.

4. Conclusions

In this study, we report the effect of potential on the growth and properties of electrodeposited zinc oxide films from using 5×10^{-2} M $ZnCl_2$ or 1×10^{-2} M $Zn(NO_3)_2 \cdot 6H_2O$ at 72 ± 2 °C and with supporting electrolyte 0.1 M KCl aqueous solutions on ITO substrates. The differences that occurred in the structural, optical and morphological were also seen. According to XRD results, the (002) peak intensity of the ZnO thin films obtained with zinc chloride are higher average 3.19 times than that of the obtained films with zinc nitrate. With regard to the transmittance spectra of the ZnO films obtained in using zinc nitrate at -0.85 V and at -0.95 V are lower average 3 times than that of the films obtained with using zinc chloride at -0.85 V and at -0.95 V. Additionally, the energy band gaps of ZnO films obtained using zinc nitrate at -0.85 V and using zinc chloride at -0.85 V have about the same. Optical band gap of ZnO varies naturally from 3.2 to 3.4 eV at room temperature [23]. But ZnO film having 3.63 eV energy band gap could be produced in this study. The surface morphologies of ZnO films prepared at different cathodic potentials were investigated

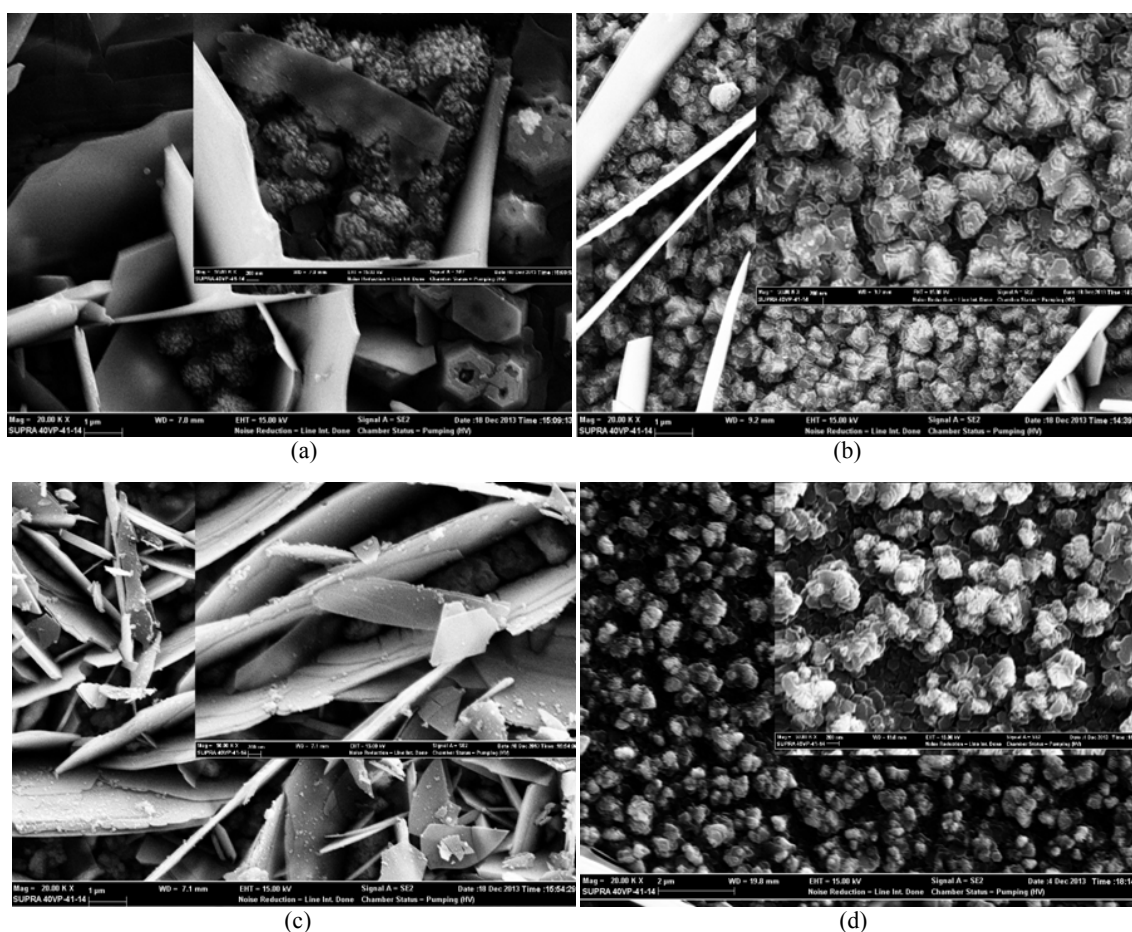


Fig. 6 Relatively low (20,000X) and high (50,000X) magnification top-view SEM images of ZnO films obtained in (a) zinc nitrate at -0.85 V, (b) zinc chloride at -0.85 V, (c) zinc nitrate at -0.95 V and (d) zinc chloride at -0.95 V.

by using SEM (Scanning electron microscopy). The surface of the ZnO film prepared using zinc nitrate exhibit flaky morphology. Also, the ZnO film having leafy grain morphology could be obtained by using zinc chloride at -0.95 V.

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Effect of Potential on Structural, Morphological and Optical Properties of ZnO Thin Films Obtained by Electrodeposition

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