

Effect of Dip Time on Electrodeposited Zinc Oxide Nanofilm

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Abstract: Nanofilms of Zinc Oxide (ZnO) were fabricated from solutions of zinc tetraoxosulphate heptahydrate, citric acid, and sodium hydroxide onto a Fluorine Tin Oxide (FTO) conductive glass by electrodeposition process. Time as bath parameter was varied. Three samples with time interval of 30 seconds, 60 seconds and 90 seconds were fabricated. Absorbance of the films was determined with the help of spectrophotometer. Other optical properties of the nanofilms were calculated using the appropriate equations from the literature. The deposited nanofilms have high absorbance in UV region and low absorbance in VIS – NIR region. Transmittance of the nanofilms is low in UV region and high in VIS – NIR region. Reflectance of the films is low throughout the UV – VIS – NIR regions. The optimal optical thickness of 270 nm was obtained at 90 seconds. The bandgap of the nanofilms obtained is between 3.30 to 3.60 eV. Average crystallite size of 43.04 nm was obtained for the deposited ZnO thin film.

Keywords: Zinc Oxide, Electrodeposition, Nanofilms, Band Gap, Optical Properties, XRD

1. Introduction

Zinc oxide is an inorganic compound with the formula ZnO. ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group. ZnO materials show an n-type electrical conductivity due to its native or intrinsic defects such as oxygen vacancies and interstitial zinc atoms [1]. Intrinsic zinc oxide thin films are highly resistive in nature, but when commonly doped with Group III elements such as Ga, In or Al, they become conducting [2]. ZnO has received great interest owing to its favorable properties such as wide band gap (3.3 eV), optical transparency, electrical and piezoelectrical properties, high electron mobility, and strong room-temperature luminescence [3]. ZnO is a cheap, abundant, chemically stable and nontoxic material that has been widely used in optoelectronic devices, photovoltaic devices and surface acoustic wave devices and sensors. Those properties are valuable in emerging applications for: transparent electrodes in liquid crystal displays, energy-saving or heat-protecting windows, and electronics as thin-film transistors and light-emitting diodes.

Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zincblende and the rarely observed cubic rocksalt [1]. The wurtzite structure is most stable at ambient conditions and thus most common. The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral, the most characteristic geometry for Zn (II). ZnO converts to the rocksalt motif at relatively high pressures about 10 GPa [4].

ZnO has a relatively large direct band gap of ~ 3.3 eV at room temperature. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. The bandgap of ZnO can further be tuned to ~ 3 – 4 eV by its alloying with magnesium oxide or cadmium oxide [4].

Many techniques have been used for depositing high quality ZnO thin films. Some of them are electrodeposition technique [5, 6], electrospinning technique [7], pulsed laser deposition [8], RF sputtering [9], chemical solution deposition [10, 11], electron beam evaporation [12, 13], the

sol – gel method [14], spray pyrolysis [15, 16], ultrasonic spray pyrolysis technique [3].

Cathodic electrodeposition technique has been recognized as the effective method for the production of metal oxide thin films, particularly ZnO thin films due to its simplicity, low temperature process, high deposition rate, low cost technique and suitability for large area substrate. This technique used a very low cathode voltage or current to produce the ZnO thin film on any conductive substrate such as a transparent conducting oxide [5] or any other metal plate [17]. In this deposition technique, the film thickness, electrical structural, morphology and optical properties can be controlled by the various deposition parameters such as: current density, applied potential, deposition time and the concentration of the electrolytic bath. In this work, ZnO thin films were electrodeposited at room temperature at varying deposition time.

2. Materials and Method

All organic reagents and solvents were purchased from Sigma-Aldrich and used without further purification. Prior to the deposition of ZnO films the solutions to be used were prepared. 0.5 M of Zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) solution was prepared by dissolving 0.434 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ salt in 100 mls of double distilled water and this solution served as Zn^{2+} ion precursor. 0.5 M of Citric acid was prepared by dissolving 0.22 g of citric acid in 100 mls of double distilled water. This solution served as precursor for oxygen. 24.50 % NH_4OH solution served as both complexing agent and pH adjuster. All FTO substrates were cleaned by ultrasonic treatment in acetone for 10 minutes. The cathodic deposition

of ZnO films was performed at 2.07V/SCE potential on the fluorine tin oxide (FTO) conducting glass substrates using the three electrodes setup of electrodeposition. The three electrodes used were the working electrode, reference electrode and the counter electrode. During the deposition, the platinum foil which served as the counter electrode was used as the anode. A saturated calomel electrode (SCE) was used as the reference electrode while the working electrode was the FTO conducting glass substrates which served as the cathode. Dazheng DC-power supply (model: PS-1502A) and two digital multimeters; Mastech (MY-68) and DT9201A CE) were used in the setup for the electrodeposition. In this experiment, three pre-treated fluorine tin oxide (FTO) conducting glass substrates were used. Each of the 3 beakers used for experiment contains various volume of the reagents used for the experiment. The three slides were labeled ZO_1 , ZO_2 , ZO_3 respectively. Each of the baths for deposition of ZnO contains 10 mls of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 10 mls of Citric acid and 5 mls of ammonium hydroxide. Zinc sulphate heptahydrate was firstly measured using a 10 mls syringe, transfer to 50 mls beaker, then 10 mls of Citric acid. Lastly, 5 mls of ammonium hydroxide was also measured and transferred to the 50 mls beaker, the mixture was stirred for 5 minute to obtain a homogeneous mixture. The ZnO films were electrodeposited for different time intervals starting with 30 seconds, 60 seconds and 90 seconds. Table 1 shows the constituents of each deposition bath. The deposited films were annealed at 573 K. Some properties of ZnO thin films such as optical and crystal structural properties of the films were determine using spectrophotometer and x- ray diffractometer.

Table 1. Chemical Constituents for Time Optimization of ZnO Thin Films.

Bath Name	Chemicals	Concentration (mol)	Volume (ml)	pH	Deposition Time (sec.)	Bath Temp. (K)
1	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.5	10.00	9.8	30	303
	Citric acid	0.5	10.00			
	NH_4OH		5.00			
2	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.5	10.00	9.8	60	303
	Citric acid	0.5	10.00			
	NH_4OH		5.00			
3	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.5	10.00	9.8	90	303
	Citric acid	0.5	10.00			
	NH_4OH		5.00			

3. Result and Discussion

The electrodeposited films are subjected to optical and structural characterization to determine their optical and structural properties. The optical properties of the film were determined using a Janway 6405 UV-visible spectrophotometer while the structure properties of the films were done using Rigaku Ultima IV X-ray diffractometer.

3.1. Optical Properties

Optical properties of the deposited films are discussed in this section. The optical properties studies include; optical thickness, absorbance, transmittance, reflectance, refractive

index extinction coefficient, band gap energy and optical conductivity. Figure 1 reveals the plot of thickness against time of deposition. This result revealed that thickness of the films increases linearly as time of deposition increases. Optimal thickness of 0.27 μm (270 nm) was obtained for film deposited at 90 seconds. Figure 2 shows the plot of absorbance against wavelength. Absorbance of the films is moderate within UV region with numerical values between 0.42 at 320 nm to 0.28 at 400 nm. These values decrease slowly within VIS – NIR region with a minimal absorbance value of 0.01 at 1100 nm for film deposited at 30 seconds. The absorbance can be seen to increase as time of deposition increases.

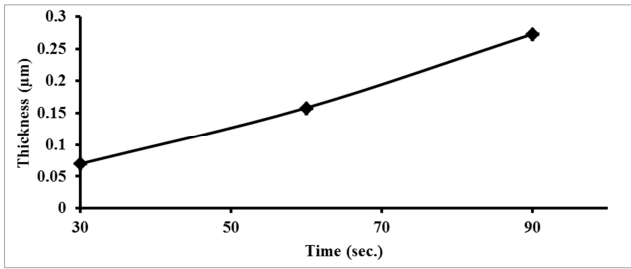


Figure 1. Plot of Thickness (μm) against Time of Deposition (sec).

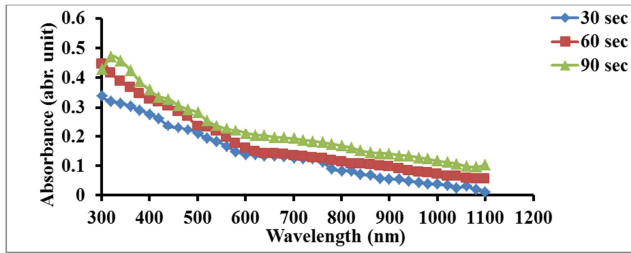


Figure 2. Plot of Absorbance (abr. unit) against Wavelength (nm).

Figure 3 shows a plot of percentage against wavelength. Transmittance values of the film within the UV region range from 33.73 % to 46.13 %. In VIS – NIR region, the transmittance ranges from 46.88 % to 97.72 %. This shows that the electrodeposited films of ZnO transmit more of VIS – NIR radiation more than UV. The transmittance decreases as time of deposition increases. Figure 4 shows the graph of reflectance of the films plotted against wavelength. In general, the films are of low reflectance ranging from 0.2 to 0.01. The reflectance decreases as wavelength increases but decreases as time of deposition increases. Figure 5 is the graph of refractive index of the deposited ZnO films plotted against wavelength. Refractive index of the films decreases as wavelength increases but increases as time of deposition increases. An optimal refractive index of 2.62 and minimal value of 1.26 were obtained for the deposited films. Figure 6 is the graph of extinction coefficient of the films plotted against wavelength. Extinction coefficient of the films decreases as wavelength increases. The values also increase as time of deposition increases. Peak value of 3.76×10^{-2} was obtained at 320 nm for films deposited at 90 seconds while the least value of 1.59×10^{-3} was obtained for film deposited at 30 seconds. These values confirmed that the absorption rate of radiation by the films is higher in UV region than in VIS – NIR regions. Figure 7 is the graph of optical conductivity of the films plotted against wavelength. Optical conductivity of the films decreases exponentially as wavelength increases. Also, optical conductivity increases slightly as time of deposition increases. Peak value of $91.86 \times 10^{12} \text{ s}^{-1}$ was obtained at 300 nm for film deposited at 60 seconds while the minimal value of $2.33 \times 10^{10} \text{ s}^{-1}$ was obtained at 1100 nm for films deposited at 30 seconds. This result shows that films of ZnO conduct optically in UV region more than in VIS – NIR regions of the electromagnetic spectrum. The optical results obtained are in agreement with the results of [11, 18].

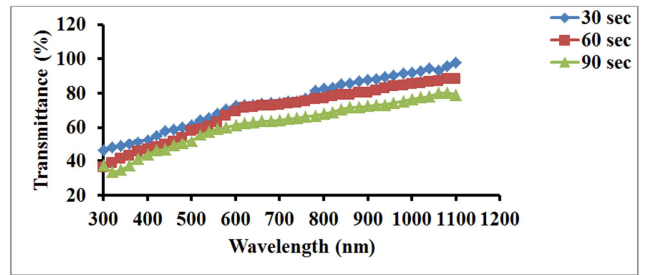


Figure 3. Plot of Percentage Transmittance against Wavelength (nm).

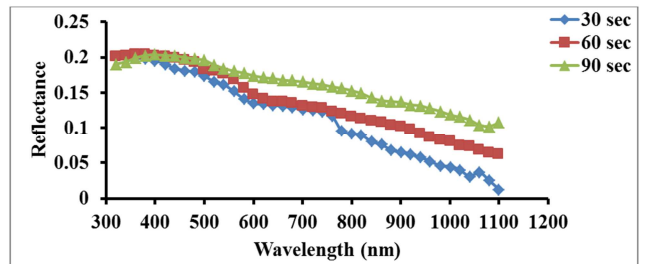


Figure 4. Plot of Reflectance against Wavelength (nm).

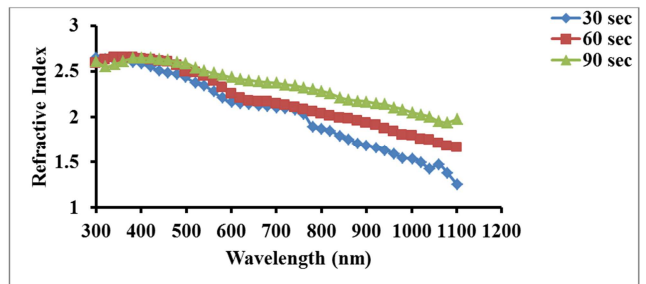


Figure 5. Plot of Refractive Index against Wavelength (nm).

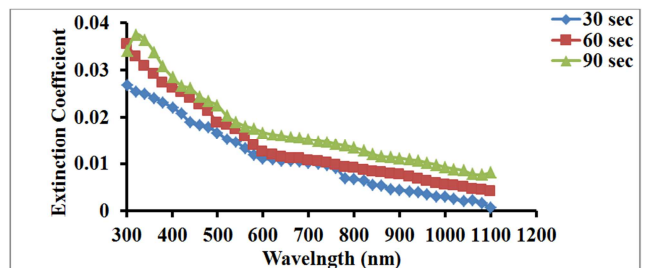


Figure 6. Plot of Extinction Coefficient against Wavelength (nm).

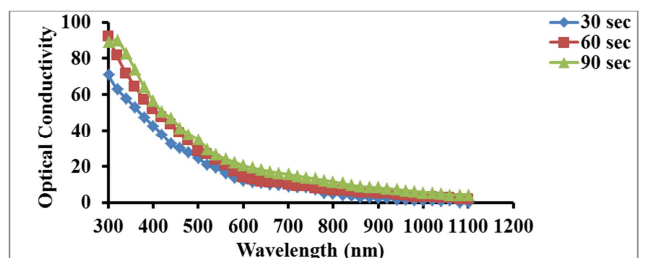


Figure 7. Plot of Optical Conductivity against Wavelength (nm).

Figure 8 shows the graph of the plot of $(\alpha h\nu)^2$ against photon energy to determine the band gap of the films. Band gap was determined by extrapolating the straight portion to the photon energy axis at $(\alpha h\nu)^2 = 0$, the band gap was

found to be between 3.30 eV and 3.60 eV. This band gap values are in line with works reviewed by [7, 18, 19].

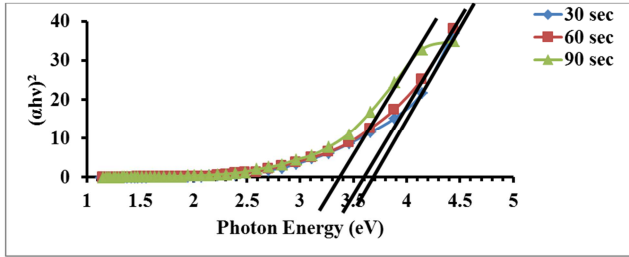


Figure 8. Plot of $(ahv)^2$ against Photon Energy.

3.2. Structural Analysis

Figure 9 shows the crystal structural studies of the ZnO nanofilm deposited at 30 seconds. The result shows (100), (002), (101), (102), (110) distinct diffraction peaks with preferred orientation in (002) plane. The film exhibits good crystallinity and all the peaks are indexed for a hexagonal phase of wurtzite ZnO with lattice constants of $a = b = 3.249\text{\AA}$, and $c = 5.206\text{\AA}$, which are in good agreement with the reported standard values (JCPDS No. 36-1451). The average crystallite size of 43.04 nm was deduced by the inverse proportional relation of the full width at half maximum (FWHM), as predicted by Debye-Scherrer's formula.

$$D = \frac{0.9\lambda}{\beta \cos \theta}. \quad (1)$$

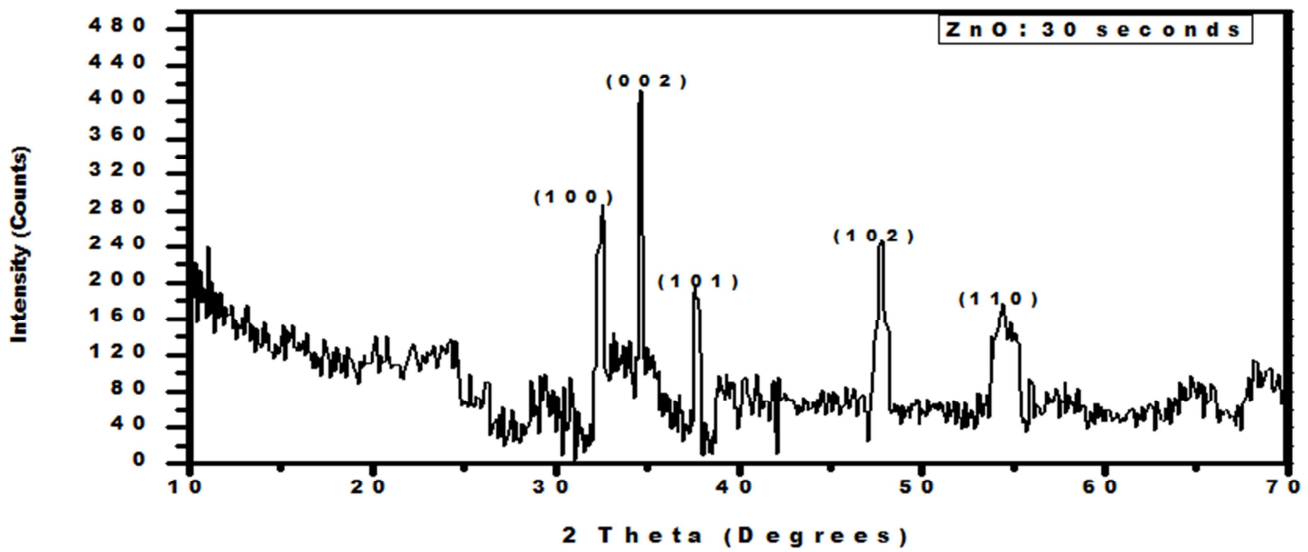


Figure 9. X – Ray Diffraction Pattern of ZnO Films Deposited at 30 seconds.

Where D is the crystalline size, λ is the X-ray wavelength used (1.5406\AA), β is the full width at half maximum (FWHM) intensity, and θ is the Bragg's angle which is the diffracting angle. The crystallite size of 43.04 nm confirmed that the deposited films of ZnO are in nanoscale. Table 1 shows the values of 2 theta angles, d – spacing and miller indices (hkl) for the deposited ZnO nanofilms.

Table 2. XRD results of Film Deposited at 30 Seconds.

2 Theta (Degrees)	d – spacing (\AA)	[hkl]
32.57	2.747	[100]
34.66	2.605	[002]
37.63	2.388	[101]
47.81	1.901	[102]
54.39	1.685	[110]

4. Conclusion

We have successfully electrodeposited nanofilms of ZnO using Zinc sulphate as precursor for zinc ion, citric acid and

24.50 % NH_4OH solution as complexing agent. The band gap of the film is between 3.30 to 3.60 eV. The films show high absorbance of about 0.47 abr. unit in UV region and high transmittance of 97.72 % in the NIR regions of electromagnetic spectrum shows that ZnO is a transparent semiconducting film. Reflectance of the film is very low in all the wavelength region. Optimal optical thickness of 270 nm. Optical is found to increase as time of deposition increases. Index reflection for the films range from 1.26 – 2.62. These optical results of deposited zinc oxide vary as the time of deposition increases. These optical properties suggest that the deposited film can be applied in thin film transistors which required a wide band gap material at room temperature and transparent in the visible region of the spectra. They are also suitable for solar cell applications. X – ray diffraction analysis of the film deposited at 30 seconds confirmed that the deposited film is zinc oxide. The crystallite size of the deposited film is 43.04 nm which suggest that the films are nano-crystalline in nature.

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