

# Structural and Optical Properties and Applications of Zinc Oxide Thin Films

## Prepared by Chemical Bath Deposition Technique

D.D.O. Eya, Ph.D.<sup>1</sup>, A.J. Ekpunobi, Ph.D.<sup>2</sup> and C.E. Okeke, Ph.D.<sup>3</sup>

<sup>1</sup> Department of Physics, Federal University of Technology, Owerri, Nigeria.  
E-mail: [eyadom2003@yahoo.com](mailto:eyadom2003@yahoo.com)

<sup>2</sup> Department of Industrial Physics, Nnamdi Azikiwe University, Awka, Nigeria.

<sup>3</sup> Department of Physics, Federal University of Technology, Owerri, Nigeria.

### ABSTRACT

Zinc oxide thin films were prepared by the chemical bath deposition technique. The films, as deposited, were a hydroxide of the metal as a result of water molecules still contained after air-drying.

Post deposition annealing of the films expelled the water molecules resulting in the ZnO. The annealing also revealed the effect of thermal treatment on the structural and optical properties of the films. The annealing temperatures used in this study were 373K, 403K, 423K, 453K, 463K, and 523K. The ZnO films showed, on average, 20% reflectance especially in the visible (VIS) and infra-red (IR) regions of the electromagnetic spectrum. The transmittance ranged between 35 and 45% for the films annealed at 453K and 523K. At higher annealing temperatures, the extinction coefficient is proportional to the wavelength. On average, the refractive index of the metallic oxide is 2.64. The band gap is 2.6eV and the grain size ranges between 0.3035 and 0.726Å. The wide band gap semiconductor has a wide range of applications in areas including acoustic wave devices, micro-electromechanical systems, band pass filters, optic waveguides, and laser deflectors using piezoelectric or piezooptic properties, etc.

(Key words: structural properties, optical properties, band gap, grain size, refractive index, annealing temperature, transmittance, extinction coefficient).

### INTRODUCTION

Zinc oxide is a wide band-gap semiconductor [Sun 1999]. Thin films of the metallic oxide have a wide variety of applications such as surface acoustic wave devices (SAW), bulk acoustic

wave devices (BAW), acoustic-optic devices, micro-electromechanical systems (MEMS), band pass filters, optical wave-guide, and laser deflectors using piezoelectric or piezooptic properties [Sun 1999, Whangbo 2000, Bao 1998, Subramanyam 2000]. With appropriate dopants such as aluminium, ZnO is electrically conductive and could be employed as transparent conducting electrodes for flat panel displays and solar cells. Due to its unique conducting mechanism based on oxygen vacancies, zinc oxide is also used in oxygen gas sensors [Bao 1998, Sun 1999].

Conducting ZnO thin films are good infrared reflectors and are applied as energy efficient window treatments where high infrared reflectance and low thermal emittance are required [Cotton and Wilkinson 1988].

In view of its wide band gap, ZnO is being used as window layers in copper indium diselenide based heterojunction solar cells to enhance the short circuit current stability in the presence of hydrogen plasma which enables use in the amorphous silicon solar cell fabrication by plasma enhanced chemical vapour deposition [Granqvist 1990, Bao 1999, Subramanyam, 2000]. It has also been recognized as a promising alternative material to transparent conducting indium tin oxide because of its low cost and non-toxicity [Subramanyam 2000]. ZnO films have also been used in many devices such as gas sensors, as high temperature solid lubricants in gas turbine engines, and in electrochromic devices.

The main property of ZnO for these applications is the polar nature of the crystalline structure of the oxide thin films [Whangbo 2000]. Various deposition techniques have been employed in the preparation of ZnO thin films such as spray

pyrolysis [Santana 1999], sputtering [Subramanyam 2000], sol-gel [Bao 1998], ionized cluster beam deposition [Whangbo 2000], epitaxial growth [Sun 1999], etc.

In recent times, much interest has been generated around the chemical bath deposition [CBD] technique. The CBD is based on controlled precipitation of the desired compound from the reaction solution [Ezema 2000, Udejaja 1996]. The technique is simple, cost effective, reproducible and the materials are readily available [Tanusevski 2003]. Another advantage of the CBD method over other methods is that the films can be deposited on different kinds, shapes, and sizes of substrates [Cruz-Vazquez 2001].

In this paper, we present a study of the optical and structural properties of ZnO thin films deposited by chemical bath deposition techniques on glass substrates with post-deposition annealing.

## EXPERIMENTAL DETAILS

ZnO thin films were prepared using the chemical bath deposition technique. The reaction bath is composed of zinc chloride ( $ZnCl_2$ ), sodium hydroxide (NaOH), and triethanolamine (TEA), which was used as complexing agent. Ammonia ( $NH_3$ ) could be used as alternative complexing agent.

The solution was made in 50ml beakers. Substrates consisted of 76mm x 26mm x 1mm commercial quality glass microscope slides. Prior to use, these glass slides were soaked in Aqua Regia, a mixture of concentrated HCl and  $HNO_3$  in the ratio of 3:1. They were removed after 48 hours and washed thoroughly in cold detergent solution, rinsed in distilled water, and drip-dried in air. The properly degreased and cleaned substrate surface has the advantage of producing highly adhesive and uniform films.

The substrate was immersed vertically at the center of the reaction bath in such a way that they did not touch the walls of the beaker. Several variations of the reaction mixture and dip times were employed to optimize and standardize the film growth conditions.

The reaction mechanism is as follows:



At the end of the dip period, the films were washed and drip-dried in the air. Some of the films were annealed at 373, 423, 453 and 523K, respectively. The composition of the ZnO films was determined by studying the energy dispersive x-ray fluorescence (EDXRF) of the samples using  $^{109}Cd$  excitation source that emits Ag-K X-rays (22.1KeV). The structural properties under various annealing temperatures were studied using x-ray diffractometer. The model used in this study was PW 1800 with a copper anode. The optical absorbance/transmittance of the films was studied in the spectral range of 340-1000 nm using a Unicam Helios Gamma UV-visible spectrophotometer.

## RESULTS AND DISCUSSION

The color of the deposited films was white when deposited as zinc hydroxide but when annealed at 403K, the films reduced to ZnO after they had lost the water content. Although thin films of the ZnO prepared using other techniques like sol-gel [Bao 1998], ionized cluster beam [Whangbo 2000], spray pyrolysis [Santana 1999], and pulsed laser deposition [Sun 1999] show the oxide film as a transparent oxide, other studies in the literature show it as a white film [Cruz-Vazquez 2001, Cotton 1988]. It needs to be borne in mind that the properties of semi-conducting thin films are not general in nature but are rather unique to the material and the technique of deposition [Chopra 1983].

The films were prepared at the optimum bath condition. The deposition parameters and thickness of the films are shown in Table 1. The relatively higher thickness for films between 300 and 373K is partly due to the presence of water molecules in the films in addition to other growth conditions.

**Table 1:** Deposition Parameters and Thickness of ZnO Thin Films.

Samp	Molar Ratio (ZnCl <sub>2</sub> : TEA : NaOH)	Volume Ratio	Dip Time (hrs)	Anneal Temp. (K)	Avg. Thickness (μm)
Z39	0.1:1.0:0.4	25:4:20	20	300	0.675
Z45	0.1:1.0:0.4	25:4:20	20	300	0.657
Z4	0.2:1.0:0.4	20:10:20	24	373	0.674
Z34	0.1:1.0:0.4	18:3:18	18	373	0.435
Z36	0.08:1.0:0.32	18:3:18	18	423	0.410
Z37	0.08:1.0:0.32	18:3:18	18	423	0.285
Z25	0.04:1.00:0.08	20:10:20	24	453	0.583
Z53	0.07:1.00:0.28	25:3:20	20	453	0.490

The chemical bath deposition technique is based on controlled precipitation of the desired compound (ZnO in this case) from the reaction solution [Ezema 2000, Udeaja 1996]. Fast precipitation implies that a thin film cannot form on a substrate immersed in the solution. However, if the reaction is slow, thin solid films of the neutral atoms could form on the substrate if the equilibrium condition of the bath is optimum.

Ions in a given reaction bath are controlled by ionic and solubility products moderated by the complexing agent. In a saturated solution of a weakly soluble compound, by the solubility product principle, the product of the molar concentrations of its ions called the ionic product is a constant at a given temperature. For a reaction of the form:



the ionic product,  $IP = [A^{y+}]^x [B^{x-}]^y = a$  constant, where the constant is the solubility product SP. Hence, the equilibrium condition provides that  $IP = SP$ . However, if  $IP > SP$ , precipitation will occur but if  $IP < SP$ , the solid phase will dissolve until the equilibrium condition is attained.

The optical transmittance (T) is related to absorbance by:

$$T = 10^{-A} \quad \text{..... (1)}$$

for weakly absorbing films on non-absorbing substrate:

$$T = (1-R)^2 \exp(-\alpha t) \quad \text{..... (2)}$$

Transmittance and reflectance as functions of wavelength are shown in Figures 1 and 2. The variation in the reflectance of the films as grown

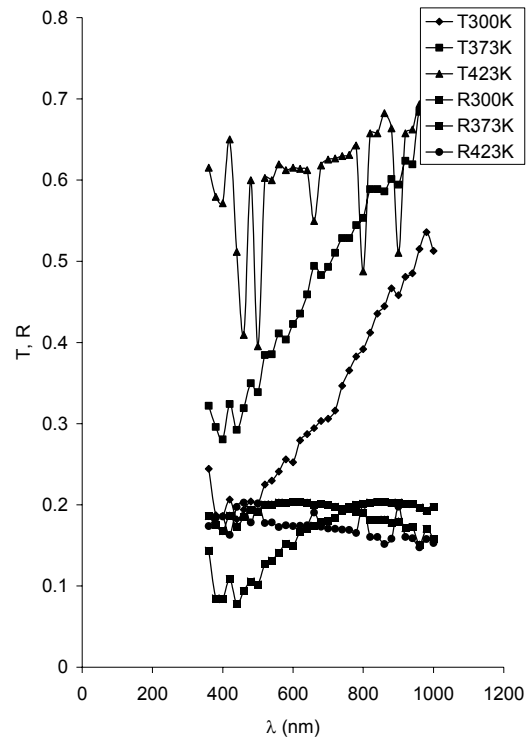


Fig. 1: Transmittance (T) and Reflectance (R) as functions of wavelength (λ) under various thermal treatments.

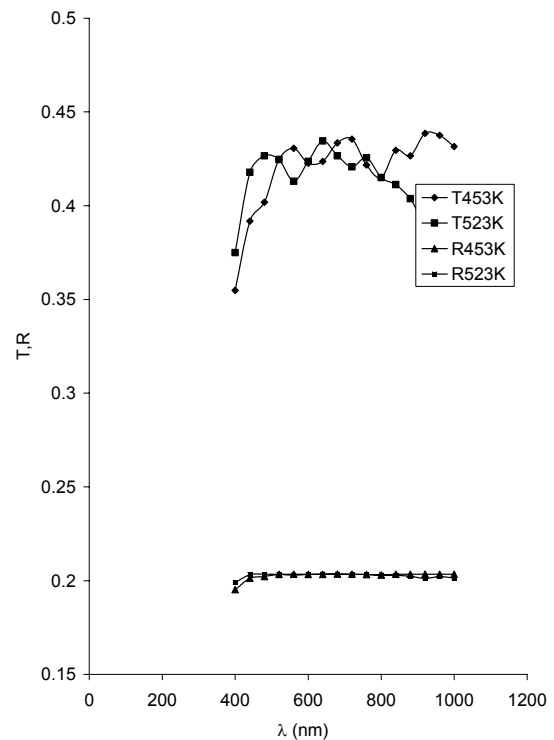


Fig. 2: Transmittance (T) and Reflectance (R) as functions of wavelength (λ) under various thermal treatments.

was as a result of the presence of water molecules in the films. The films annealed at 373K and above showed reflectance of 20% on the average in all regions of the solar spectrum (UV – IR). The transmittance of the films at 300 and 373K varies almost linearly with wavelength. However, the transmittance of the films annealed at 423K and higher temperatures show a very narrow range of variation. In Figure 2 for instance, the minimum and maximum values are 35% and 43% respectively.

The ZnO films or the films annealed at higher temperatures show exponential decay of absorbance with increasing wavelength as shown in Figure 3.

Variation of the extinction coefficient with wavelength shown in Figure 4 for films annealed at 453 and 523K shows a steep linear relationship indicating sharp increases in the absorption with increasing wavelength. This conforms to the relation:

$$K = \frac{\alpha \lambda}{4\pi} \dots\dots\dots (3)$$

where K is the extinction coefficient,  $\alpha$  the absorption coefficient, and the wavelength ( $\lambda$ ).

The reflectance at normal incidence can be expressed in terms of the optical constants n and k as follows [Ravich 1970]:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \dots\dots\dots (4)$$

where n is the refractive index. In the range of frequencies in which the films are weakly absorbing,  $K^2 \ll (n-1)^2$ , the following can be expressed:

$$R = \frac{(n-1)^2}{(n+1)^2} \dots\dots\dots (5a)$$

or,

$$n = \frac{(1 + R^{1/2})}{(1 - R^{1/2})} \dots\dots\dots (5b)$$

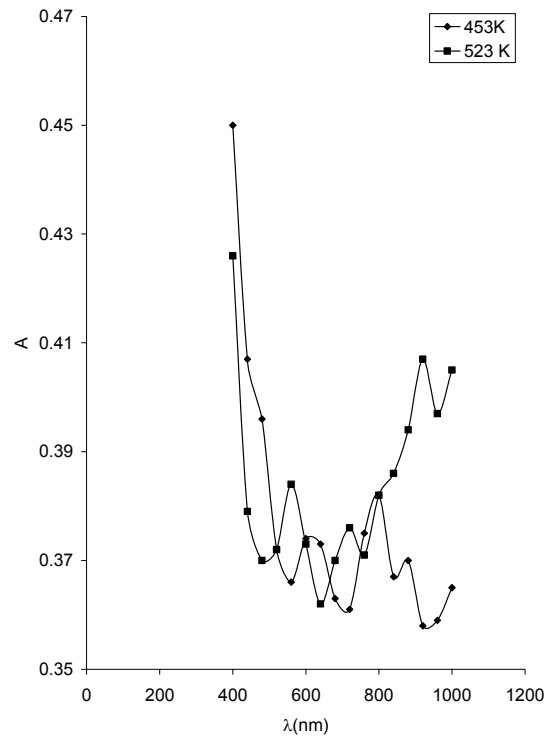


Fig. 3: Absorbance (A) as a function of wavelength ( $\lambda$ ) under various thermal treatments

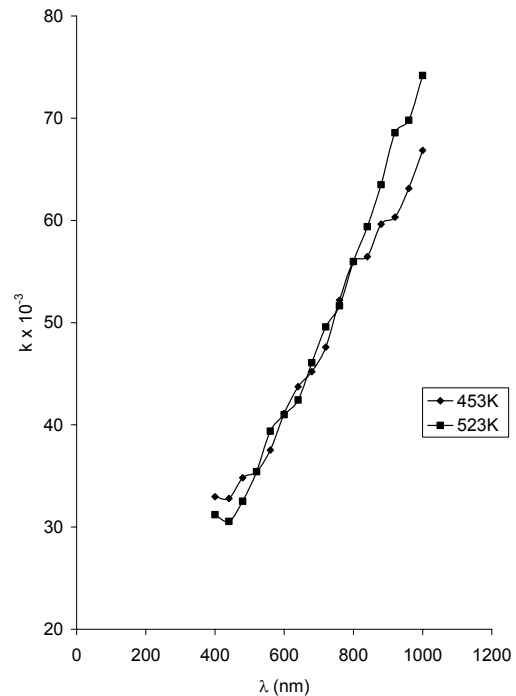


Fig.4 : Variation of extinction coefficient (k) with wavelength ( $\lambda$ ) under various treatments.

Figure 5 shows the variation of refractive index of ZnO with wavelength. The films annealed at higher temperatures, especially those annealed at 453 and 523K, show that the refractive index remained, on average, at 2.64 in both visible and NIR regions as is shown in Figure 5. In the UV region, n seems to rise from a lower value to this maximum.

That the refractive index of ZnO is 2.64 means that electromagnetic radiation is 2.64 times slower in the oxide films than in the free space. In the high photon energy region, the energy dependence of the absorption coefficient,  $\alpha > 10^4 \text{cm}^{-1}$  suggests the occurrence of direct optical transition. The direct transition dependence on photon energy is given by the relation [Tanusevski 2003, Thangaraju 2000]:

$$(\alpha h\nu) \propto (h\nu - E_g)^{1/2} \quad \text{..... (6)}$$

where  $\alpha$  is the absorption coefficient,  $\nu$  is the photon frequency, and  $E_g$  is the material band gap.

The band of the metallic oxide was determined by plotting  $(\alpha h\nu)^2$  as a function of  $h\nu$ , and extrapolating the linear portion of the curve to  $(\alpha h\nu)^2 = 0$  as shown in Figure 6. The value obtained for the optical band gap is 2.6eV.

The results of our structural studies of the ZnO films were done with x-ray diffraction (XRD) and show (101), (110), (011) and (111) distinct diffraction peaks for the films grown in this study, as shown in Figure 7a.

The intensity of the peaks increased with increasing annealing temperatures. For the samples annealed at 403 and 463K we have identified (101), (110), (011), (111) and (011) peaks respectively as shown in Figures 7b and 7c.

The grain size (D) was estimated from Scherrer's formula [Gomez 1999, Van Huis 2003]:

$$D = \frac{K\lambda_x}{\beta \cos \theta} \quad \text{..... (7)}$$

Where K is a dimensionless constant,  $2\theta$  is the diffraction angle,  $\lambda_x$  is the x-ray wavelength, and  $\beta$  is the full width at half maximum (FWHM) of the diffraction peak.

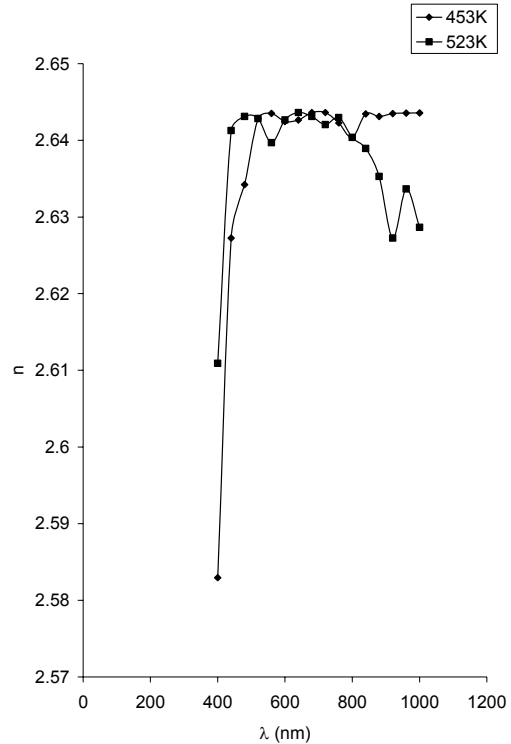


Fig. 5: Refractive index (n) as a function of wavelength ( $\lambda$ ) under various thermal treatments.

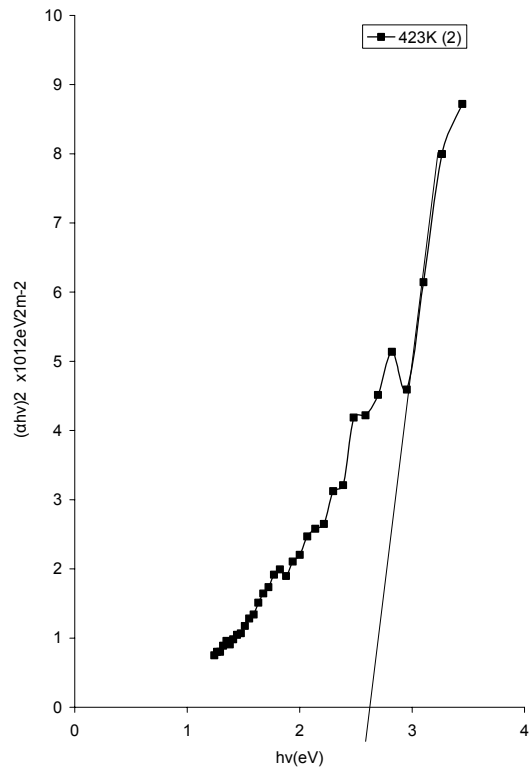
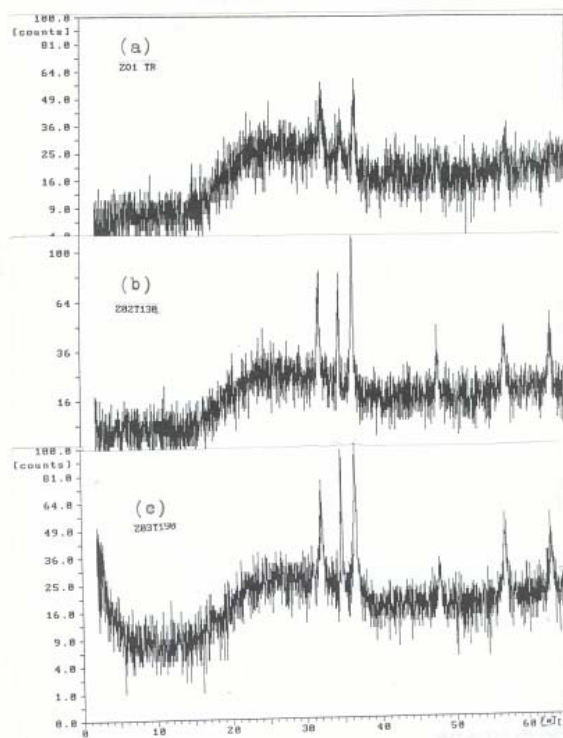


Fig. 6: A plot of  $(\alpha h\nu)^2$  as a function of photon energy ( $h\nu$ ) for ZnO.



**Figure 7.** X-Ray Diffraction Spectra for ZnO Films Annealed at Different Temperatures

The grain size corresponding to the various diffraction peaks or reflection planes are shown in Table 2.

**Table 2:** Deposition Parameters and Thickness of ZnO Thin Films.

Diffraction peaks	D values for Z01 (nm)	D values for Z02 (nm)	D values for Z03 (nm)
101	0.4868	0.4867	0.3607
110	0.4809	0.7264	0.7266
011	0.4842	0.4123	0.4810
111	0.4505	0.3941	0.3154
$\bar{1}\bar{1}\bar{1}$		0.3256	0.3620
$0\bar{1}\bar{1}$		0.7584	0.3035

## CONCLUSION

Zinc oxide thin films have been successfully prepared by the chemical bath deposition technique. The disparity between the properties of the films as grown and those annealed at higher temperatures is as a result of water

molecules still contained in the films as deposited. On average, ZnO shows a reflectance of 20% in all regions of the electromagnetic spectrum. The minimum and maximum reflectance is 35% and 43% respectively. It also shows a refractive index of 2.64 and a band gap of 2.6eV. The range of the grain size is 0.3035nm to 0.7266nm.

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#### ABOUT THE AUTHORS

**D.D.O. Eya, Ph.D.** is an academic staff member in the Department of Physics at the Federal University of Technology in Owerri, Nigeria. His research interests are in the areas of photovoltaics, thin film deposition, and characterization.

**A.J. Ekpunobi, Ph.D.** serves as the Head of the Department of Industrial Physics at Nnamdi Azikiwe University in Awka, Nigeria. His research interests include photovoltaics, thin film deposition and characterization, and optical technology.

**C.E. Okeke, Ph.D., FAS** is a professor of Solid State Physics and a member of the academic staff of the Department of Physics and Astronomy at the University of Nigeria, Nsukka. His research interests include photovoltaics, thin film deposition and characterization, and biomass energy conversion.

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