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Effect of Molar Concentrations on the Structural and Optical Properties of Zinc Oxide Thin Films

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Abstract

Thin films of zinc oxide (ZnO) were deposited on soda-lime (glass) substrate using chemical bath deposition (CBD) technique. The structural and optical properties of the deposited films were investigated using X-ray diffractometer (XRD) and UV- spectrophotometric measurements. The absorption data were used to determine the energy band gap and other optical parameters. It was observed that the films were polycrystalline in nature with high optical transmittance. The energy band gaps were found to vary between 3.09 and 3.45 eV using the absorption spectrum fitting (ASF) method. The influence of molar concentrations on the extinction coefficient, refractive index, real and imaginary dielectric constants was also discussed. The study shows that the optical parameters were greatly influenced by the molar concentrations.

Keywords: Band gap; zinc oxide; Refractive index; Optical; Thin films.

I. Introduction

Generally, the production of energy and its consumption have been a basic factor in the development of human society. The consumption of energy is strongly related with world population growth as well as characteristics of modern society like life expectancy, access to water and electricity, etc. [1-3]. The world energy production is mainly achieved by burning fossil fuels such as coals, natural gas and petroleum. However, the use of fossil fuels has raised serious concern due to its limited availability and environmental issues [1]. The finite and polluting nature of fossil fuels have necessitated an urgent need for a renewable and eco-friendly sources of energy such as solar, wind, water, geothermal, ocean and bio-energy [4-6]. Among the various forms of renewable energies, solar energy is a more efficient source of eco-friendly energy that has been fully developed by researchers to convert sunlight into useful electrical energy [4]. The energy from the sun is free, inexhaustible, re-useable, and clean [7]. In Nigeria, where daily sunshine is very massive, the possibility of solving her energy problem through photovoltaic (PV) or solar conversion is high [8]. In recent times, thin film technology has provided an opportunity for researchers to delve into solar energy research due to their low cost of production, tunable band gap and the ease of forming electron-hole pair to convert photons to electricity [9-13].

In recent times, zinc oxide (ZnO) thin films have attracted much attention due to their unique structural, optical and electrical properties. Thin films of ZnO are suitable for various devices such as photo-detectors, infrared detectors, sensing devices and solar cells fabrication [14, 15]. It is an ideal candidate for making cost effective (hybrid) window layers for solar cells productions having exhibited excellent optical properties; high absorption coefficient (~105 cm-1), good carrier concentrations and hole mobility [16]. Besides these properties, theoretical calculations have indicated a realistic

conversion efficiency of above 20% for ZnO-based hetero-junction solar cells [17]. However, the maximum efficiency ever reported for ZnO-based materials is far below 5 % due to low efficiency [17]. To enhance the efficiency of ZnO-based hetero-junction, several metal dopants (indium, copper, bismuth, silver, antimony, iron, lead, etc.) have been added as well as the utilization of various deposition techniques [1, 14-16].

Several deposition techniques have been employed to synthesize ZnO thin films such as sputtering, chemical vapor deposition (CVD), molecular beam epitaxy (MBE), pulse laser deposition (PLD), spray pyrolysis, sol-gel process and chemical bath deposition (CBD) [14, 15].

In the present work, chemical bath deposition (CBD) technique was used to synthesize zinc oxide (ZnO) thin films. Our aim is to develop a better growth approach of new and eco-friendly thin films materials for the production of low cost solar cells. Improvement in the properties of ZnO thin films due to the deposition technique will play a major role in enhancing the device efficiency. Particularly, this communication is concerned with the influenced of molar concentrations on the structural and optical properties of ZnO thin films deposited by CBD technique which hitherto has not been studied using this route.

II. Materials and Method

A. Materials

To synthesis ZnO thin films, chemicals of analytical grade (AR) were used without further purification and they include; ammonia solution (NH_3), sodium hydroxide (NaOH), ethylenediamine acetic acid (EDTA), zinc chloride ($ZnCl$) and distilled water.

B. Method

1) Zinc oxide (ZnO) Thin Films Preparation

Clean substrates (washed in detergent solution, ethanol and distilled water respectively) were used for the deposition of zinc oxide (ZnO) thin films at room temperature. Zinc chloride ($ZnCl_2$) was used as a source of zinc ions (Zn^{2+}). For 0.03 M of ZnO film thin, 4.5 ml of zinc chloride (0.4 M) was used. Under continuous stirring, 2 ml of ammonia solution (5 M) was added, followed by slowly introducing 5 ml of sodium hydroxide (2.5 M), and 16.5 ml of ethylenediamine acetic acid (EDTA) 0.2 M. The mixture was then topped to 60 ml level by the addition of 32 ml of deionized water. The different zinc oxides molar concentrations of 0.04 M, 0.05 M and 0.06 M were prepared in similar manner. The required volume of ammonia solution (ligand) was then added in order to obtain pH value of 10. Each bath was allowed to stand for a fixed deposition period of one hour. After deposition, the substrates were dried in air. The resulting chemical reactions are shown below:

$$ZnCl_2 + NH_3 \rightarrow [Zn(NH_3)]^{2+} + 2Cl^-$$

$$[Zn(NH_3)]^{2+} \rightarrow Zn^{2+} + NH_3$$

$$NaOH \rightarrow Na^+ + OH^-$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O$$

Thus, the overall reaction for the formation of ZnO thin films is given as:

$$ZnCl_2 + NH_3 + 2NaOH \rightarrow ZnO \downarrow + NH_3 + 2NaCl + H_2O$$

2) Characterization of ZnO Thin Films

The X-ray diffraction (XRD) pattern of the deposited zinc oxide thin films was observed via a (Bruker D8) X-ray diffractometer at a radiation of 1.5406Å. The UV-1800 Spectrophotometer in a wavelength range of 300 to 1000 nm was used to determine the optical properties of the material. The optical band gaps (E_g), extinction coefficient (k), refractive index (η) and dielectric constants were estimated from the optical data.

III. Results and Discussion

A. XRD Analysis

The X-ray diffraction (XRD) pattern of the prepared ZnO thin films is indicated in Fig. 1, where the emergence of four main diffraction peaks at 15.19°, 19.78°, 22.94°, and 30.66°, which corresponds to (100), (002), (101), and (102) planes were clearly observed. The presence of these peaks indicates that the deposited ZnO thin films are polycrystalline in nature [18]. Increasing the molar concentrations from 0.03 to 0.04 M shows that the intensity of the peaks decreased drastically, thus, indicating a transformation in the crystallinity orientation of the deposited ZnO thin films. However, the intensity of the peaks becomes stronger and bigger with further increase in molar concentrations (0.5 and 0.6 M). This result could be attributed to the variations in the film's chemical reactivity during the formative stages [18].

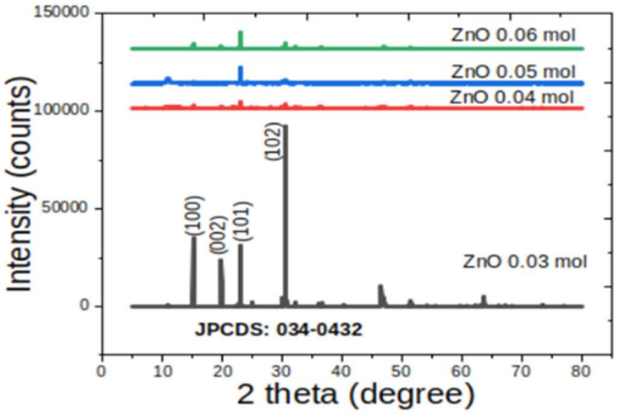

Fig. 1 XRD pattern of ZnO thin films.

B. Optical Characterization

Fig. 2 shows the optical absorbance spectra of the deposited ZnO thin films. In all the films, it was observed that the shapes of the curves were similar with differences in absorbency, with the films having high absorbance around the ultraviolet region (300 – 350 nm), which decreases consistently as wavelength increases. The high absorbency in this region may be attributed to the effects of light scattering from the nano-sized grains of the films due to variations in the molar concentrations [19].

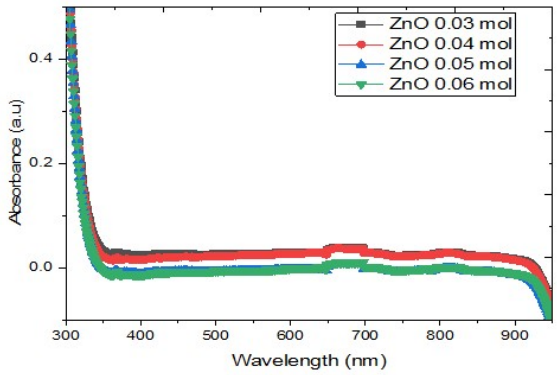

Fig. 2 The absorption plot of ZnO thin film

Fig. 3 shows the plot of transmittance against wavelength of ZnO thin films. The plot showed a significant increase in the transmitting properties of all the films with wavelength. Similar observations have been reported in literature for binary thin films [14, 20]. The high transmittance with considerably increase in wavelength could arise from the low scattering nature of the deposited ZnO thin films [21]. The increased transmittance within the wavelength range makes ZnO a good conducting material for several optoelectronic applications [2, 19].

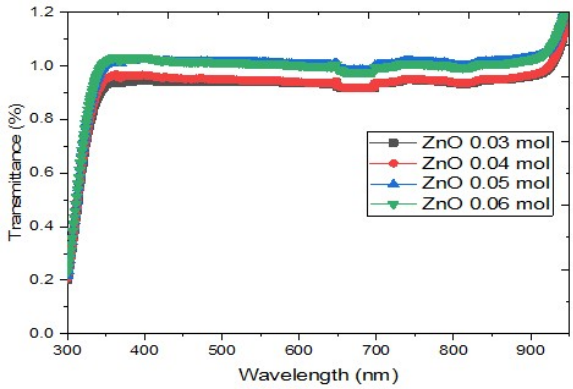

Fig. 3 The transmittance plot of ZnO thin film

The band-gap was evaluated using (1). Where the absorption coefficient $\alpha(v)$ and the photon energy (hv) is related by the expression in (1) [13]:

$$\alpha(v)hv = B(hv - E_g)^n \quad (1)$$

Here E_g, is the optical band gap, hv is the photon energy and B is a constant which depend on the transition probability [2]. Also, from (1) the index (η) known as the power factor of the electronic transition mode assumed values between $^1/_2$ and 3 depending on the nature of the material. Exponent $n = {}^1/_2$ for allowed direct transitions, $n = 2$ for allowed indirect transitions, n = 3/2 for forbidden direct transitions and $n = 3$ for forbidden indirect transitions [13, 18]. Introducing the absorption spectrum fitting (ASF) method, the optical band gap can be determined using (2) [22]:

$$E_{g(ASF)} = \frac{hc}{\lambda_g} = \frac{1239.83}{\lambda_g} \quad (2)$$

Where h is the Planck's constant, c is the speed of light and λ_g is the wavelength of the corresponding band gap. Employing the Beer – Lambert's law, (1) can be re-arranged as a function of wavelength (λ) as indicated in (3) [23]:

$$A(\lambda) = K_1\lambda\left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right)^n + K_2 \quad (3)$$

Where, the Beer-Lambert's functions $K_1 = [B(hc)n - 1\, d/2.303]$ and K_2 is a constant that is related to the reflectance of the material [23]. Using (3), one can determine the optical band gap of the deposited material in electron volts without considering the thickness. The band gap is determined by plotting $(A/\lambda)^2$ against $(1/\lambda)$ as indicated in Fig. 4 $(for\ 0.05\ Mol)$. By extrapolating the linear part of the curve at $(A/\lambda)^2 = 0, (1/\lambda_g)$ can be estimated which is then used to calculate its band gap using the relation $E_{g\,(ASF)} = 1239.83/\lambda_g$ [2, 22].

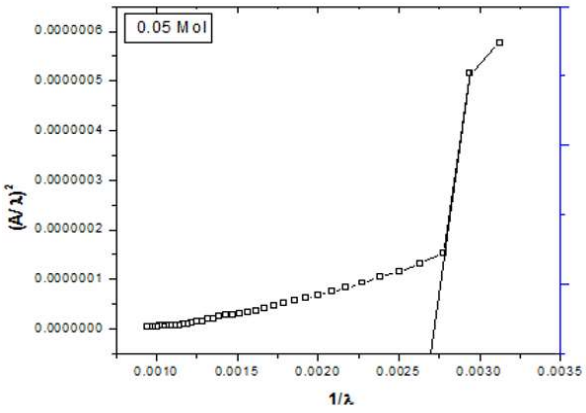

Fig. 4 The ASF plot of ZnO thin film at 0.05 Mol.

Values of the band gap are indicated in Table I. Commonly, numerous factors are responsible for the variation in the

estimated band gap values. The band gap variation may be due to the nature of the deposited ZnO thin films [21]. Also, the band gap variation may be a result of variations in transition tail width and shift effect which can be explained in terms of carrier concentrations [21].

The extinction coefficient (k) was calculated using (4) [19, 21]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

Where, α is the absorption coefficient and λ is the wavelength of the spectrum. The plot of k against photon energy is illustrated in Fig. 5. It was observed that k varies with photon energy as well as with molar concentrations for all the films as showed in Table I. Usually, the estimated values of k were generally low over the photon energy (eV) regions, consequently losing very low absorption energy down the regions [19].

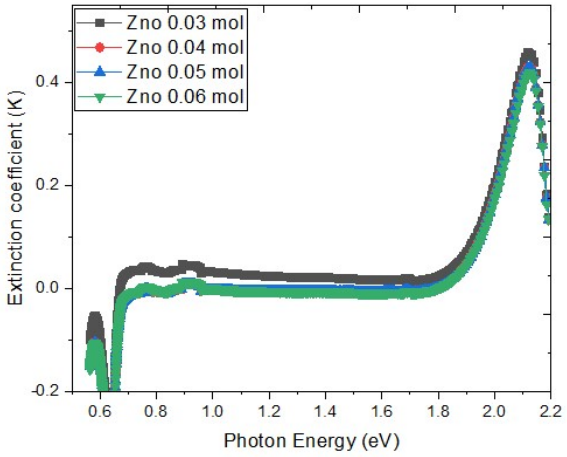

Fig. 5 Extinction Coefficient and photon energy of ZnO thin films

The refractive index (n) is one of the fundamental properties of semiconducting materials that is closely related to the electronic polarization of ions and the local field [13]. It is an important factor in determining the electronic applications of materials in optical switches, waveguides, filter, solar cells, etc. [18, 21]. Usually, the refractive index can be estimated using (5) [21]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\left(\frac{4R}{(1-R)^2}\right) - k^2} \quad (5)$$

The parameters R and k are the reflectance and the extinction coefficient. The graph of n against the photon energy is shown in Fig. 6. From the curve, it is seen that the average refractive index increased with the photon energy. However, as the molar concentration is increased, the refractive indexes were found to vary within the range of 1.102 and 1.132 (Table I). These changes exhibited by the films may be due to the trapped photon energy within the Zn-O system of the material [13, 18].

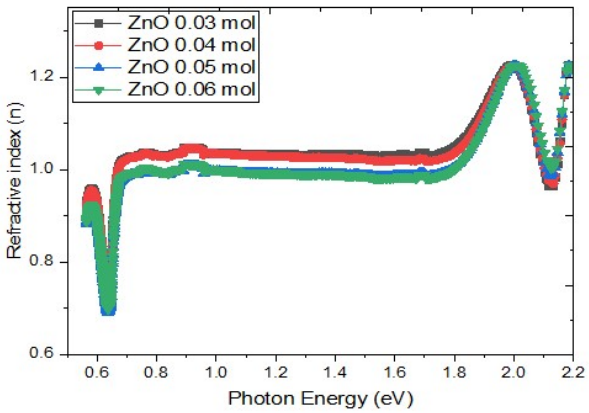

Fig. 6 Refractive Index and photon energy of ZnO thin films

The real (ε_r) and imaginary (ε_i) parts of the dielectric constants were determined using (6) and (7) [24, 25].

$$\varepsilon_r = \eta^2 - k^2 \quad (6)$$

$$\varepsilon_i = 2nk \quad (7)$$

The variations of the real and imaginary parts of the dielectric constants are illustrated in Fig. 7 and 8 respectively. It was observed that the values of the real dielectric constants were higher than the imaginary dielectric constants (Table I). However, both parts were increasing with photon energy. Similar trends have been outlined in literature for crystalline semiconductor thin films [4, 21, 25], and may be linked to the relationships between the real constant (ε_r), refractive index (n) and the extinction coefficient (k) as shown in (6) [21]. The variations in the imaginary dielectric constant are due to the energy-absorbing nature of the deposited ZnO thin films [21].

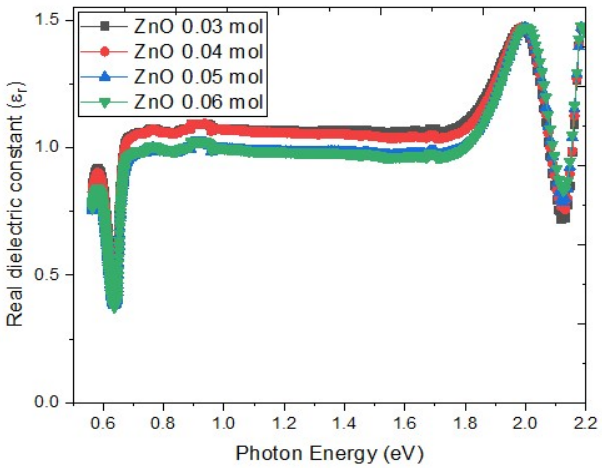

Fig. 7 Real dielectric constant and photon energy of ZnO thin films.

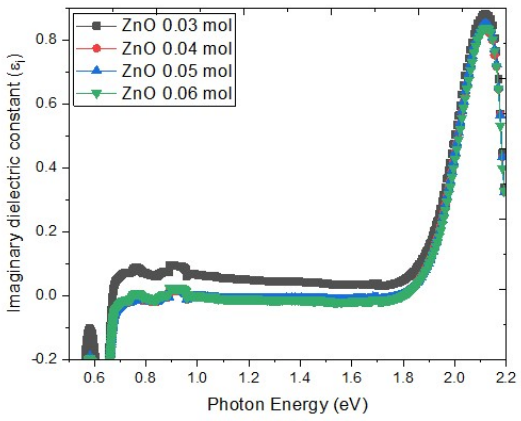

Fig. 8 Imaginary dielectric constant and photon energy of ZnO thin films.

A general representation of results obtained is displayed in Table I.

Table I. optical properties of ZnO thin films

Samples (Mol)	Band gap (eV)	Extinction Coefficient	Refractive index (η)	Dielectric Constants	
				ε_r	ε_i
0.03	3.37	0.231	1.102	1.121	0.452
0.04	3.09	0.272	1.134	1.123	0.442
0.05	3.34	0.221	1.111	1.124	0.447
0.06	3.41	0.232	1.132	1.118	0.432

IV. Conclusion

Zinc oxide thin films have been deposited on soda-lime substrates via the CBD technique at room temperature. The XRD measurements indicated that the deposited ZnO thin film is polycrystalline in nature. Optical measurement revealed that the films exhibited a high transmittance with band gap energy that varies from 3.09 to 3.45 eV with molar concentrations. The refractive index, extinction coefficient and dielectric constants were also influenced by the molar concentrations.

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