

ON THE OPTICAL DISPERSION PARAMETERS OF THIN FILM Al³⁺ DOPED ZnO TRANSPARENT CONDUCTING GLASSES

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In this work, we present the results of the optical dispersions of undoped and Al³⁺ doped ZnO glassy thin films. The films transmission spectra were measured by spectrophotometry and film compositions were obtained using Rutherford backscattering spectrometry. Results show that the refractive index dispersion data obeyed the single oscillator model. The calculated static refractive index n_s , and high frequency dielectric constant ϵ_∞ values reduced on Al³⁺ doping. The oscillator energy E_0 , oscillator strength E_d , optical spectra moments M_{-1} and M_{-3} were observed to increase on Al³⁺ doping. Reasons for these variations are attributable to grain boundaries enhancement induced by Al³⁺ incorporation. These results are considered useful for further understanding of the electronic structure of these materials.

(Received December 12, 2009; accepted December 20, 2009)

Keywords: Al-doped ZnO, Film, Dispersion parameters, Transparent glass

1. Introduction

Zinc oxide thin films are widely known to exhibit a variety of properties such as: semiconducting (II-VI), photoconducting, piezoelectricity, acousto-optical properties, transparency in the infrared region, and opto-electrical properties [1-3]. This makes thin films of ZnO very interesting materials for theoretical and experimental investigations. They have been recently studied as materials for chemical sensors for ammonia gas [4], alcohol [5] and Hydrogen [6]. ZnO is known to exhibit electrochemical stability with wide band gap energy ranging between 3.2eV and 3.4eV at room temperature [3].

Also, composites and doped ZnO optical thin film materials have received a significant amount of interest in order to relieve some of their material constraints by modifying some of their existing structures. For instance, doping of ZnO using Mn offers an interesting way to alter various properties [1, 2], for example the band gap of host material can be turned from 3.37eV to 3.70eV [7]. Glassy ZnO thin films have been deposited by a variety of techniques such as sputtering, molecular beam epitaxy, spray pyrolysis and chemical deposition. Among the thin films deposition methods, chemical bath deposition (CBD) from aqueous solutions is the simplest and most economical one. CBD method also offers the opportunity of doping the host ions with impurities on different kinds, shapes and sizes on substrates. The evaluation of optical dispersions and other optical constants of semiconductors are of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design. This has proved to be very useful for elucidation of the electronic structure of these materials [8].

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Therefore, in this work, we report the optical dispersion parameters of undoped ZnO and Al doped ZnO glassy thin films. We employed the Wemple and DiDomenico single oscillator model to calculate the oscillator constants of both the undoped ZnO and Al doped ZnO thin films.

2. Experimental

The synthesis of ZnO thin films was carried out from a controlled chemical reaction between Zn(TEA)Cl₂ complex and sodium hydroxide. The Zn(TEA)Cl₂ (TEA: triethanolamine), slowly released the zinc ions, which was hydrolyzed by sodium hydroxide. The Al doped ZnO thin films were synthesized as follow: 1.0 ml of a 0.012 M AlSO₄ aqueous solution was added to 25 ml of a 1.0 M ZnCl₂ aqueous solution. Then, 40 ml of a 1 M NaOH aqueous solution were added and stirred before the addition of deionised water to make up the bath to 50 ml. A pre- cleaned glass slide was immersed into the bath and was allowed to stand for 20hrs at room temperature (373K). White thin films on the substrates were obtained from this solution. The films were removed from the solution, washed with deionized water, dried and annealed in an oven at 473K for 20 minutes.

The optical transmissions of the films were performed with a Jenway 6403 UV-VIS spectrophotometer. Thin film compositions and thicknesses were determined with a 2.2 MeV ⁴He⁺ ion beam tandem accelerator with Rutherford backscattering (RBS) detector.

3. Results and discussion

The compositions of the films were determined using Rutherford's backscattering spectrometry. A tandem accelerator ion beam analysis having Rutherford cross section detector was used. The primary ion of the beam was alpha particles ⁴He⁺ of incident energy 2.2eV. The RBS plot of Al doped ZnO thin film glass is shown in fig. 1. The straight line is the simulated result while dotted line represents the RBS spectrum of Al doped ZnO thin films on soda lime glass. The RBS analysis revealed that the thin films on glass matrix are stoichiometric with the percentage compositions of Al: Zn: S ratio confirmed to be 10: 10: 80.

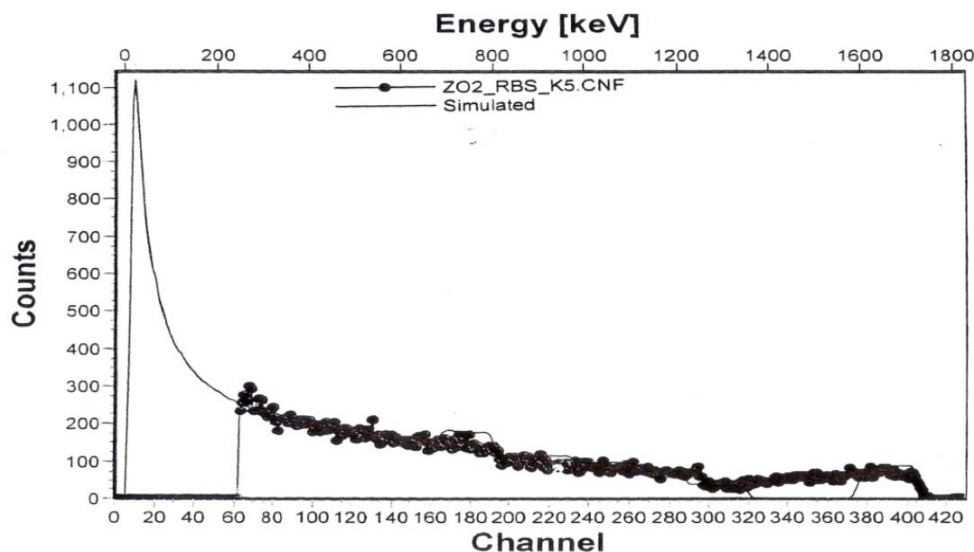


Fig. 1: RBS spectrum of Al₁₀Zn₁₀O₈₀ thin film glasses

The spectral dependence of transmittance of ZnO and Al doped ZnO thin films were measured in the wavelength range of 200-1100 nm (fig.2). Analysis of optical transmission spectra is one of the most productive tools for understanding and developing the band structure and energy band gap, of both

amorphous and polycrystalline materials. The transmission spectra of ZnO thin films show high transmission >70% at the VIS- NIR region. This transmission however dropped at < 50% at the band edge on Al³⁺ incorporation. The decrease in optical transmission of Al doped ZnO thin films can be due to the enhancement in the grain boundaries which was achieved during doping.

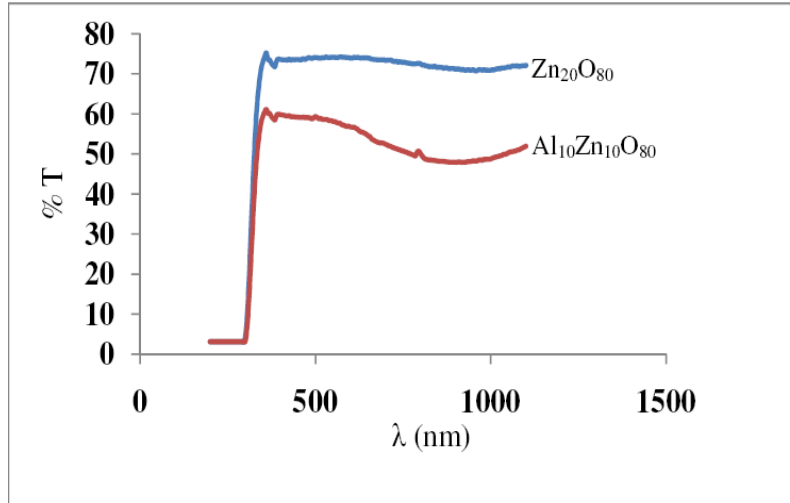


Fig. 2: Transmission spectra of Zn₂₀O₈₀ and Al₁₀Zn₁₀O₈₀ thin film glasses

The relation between absorption coefficient (α) and incident photon energy ($h\nu$) can be written as;

$$\alpha = \frac{A(h\nu - E_g)^m}{h\nu} \quad (1)$$

Where A is a constant and E_g is the band gap of the material. The values of m depends upon the type of the transition; which may have values 1/2, 2, and 3/2 corresponding to the allowed direct, allowed indirect, and forbidden direct transitions respectively [12]. From the above equation, it is clear that the plot of $(\alpha h\nu)^2$ versus $h\nu$ (fig. 3), will indicate a divergence of an energy values, E_g where the transition takes place. The values of optical band gap energies E_g were obtained by extrapolating the straight portion to the $h\nu$ axis at $(\alpha h\nu) = 0$.

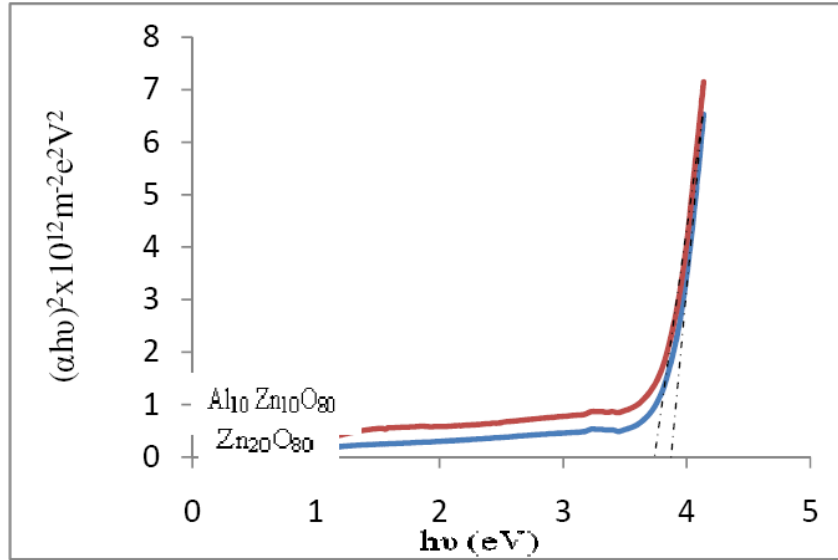


Fig.3: The plots of the variations of $(\alpha h\nu)^2$ vs. $(h\nu)$ for the thin films.

The refractive index as a function of incident photon energy (Fig. 4) was calculated using the Swanepoel’s extrapolated wavelength method as have been used by many authors [8- 10]. The refractive index tends to decrease for both both films as we approach longer wavelength regime. The refractive index was found to decrease after Al incorporation in ZnO matrix.

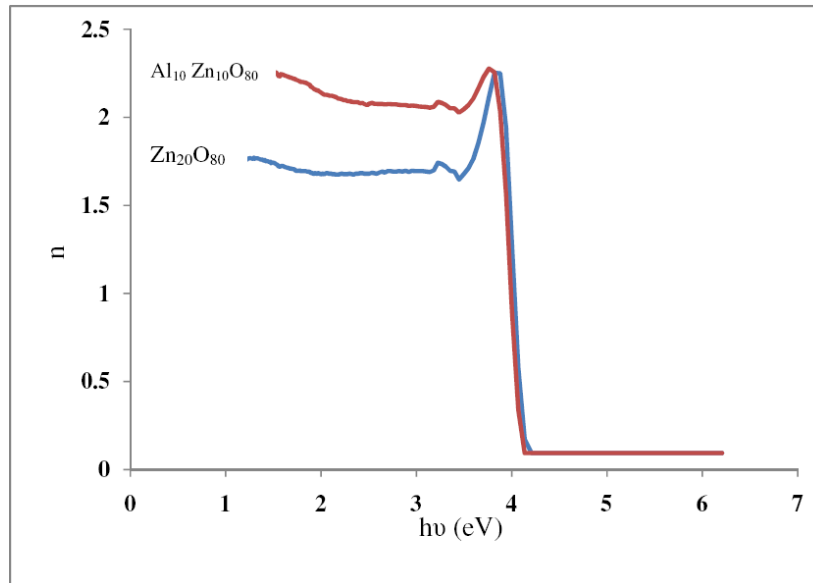


Fig. 4: Refractive index as a function wavelength for Zn₂₀O₈₀ and Al₁₀Zn₁₀O₈₀ thin film glasses

The spectral dependence of the refractive index of many semiconductors [11] can be evaluated by using the single oscillator model proposed by Wemple and Di Domenico viz;

$$n^2 = 1 + \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \quad (2)$$

Where n is the refractive index, E_0 is the average excitation energy known as the oscillator energy, E_d is the dispersion energy called the oscillator strength, and $h\nu$ is the incident photon energy. To evaluate the oscillator parameters, a graph of $(n^2 - 1)^{-1}$ against $(h\nu)^2$ was plotted in fig. 5. Where, $\left(\frac{E_0}{E_d}\right)$ represents the intercept on the vertical axis and $(E_0 E_d)^{-1}$ is the slope of the plot. Hence, E_0 , E_d , can be readily evaluated. The moments of the optical dispersion spectra M_{-1} and M_{-3} , can be evaluated using the relationships;

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \quad (3)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (4)$$

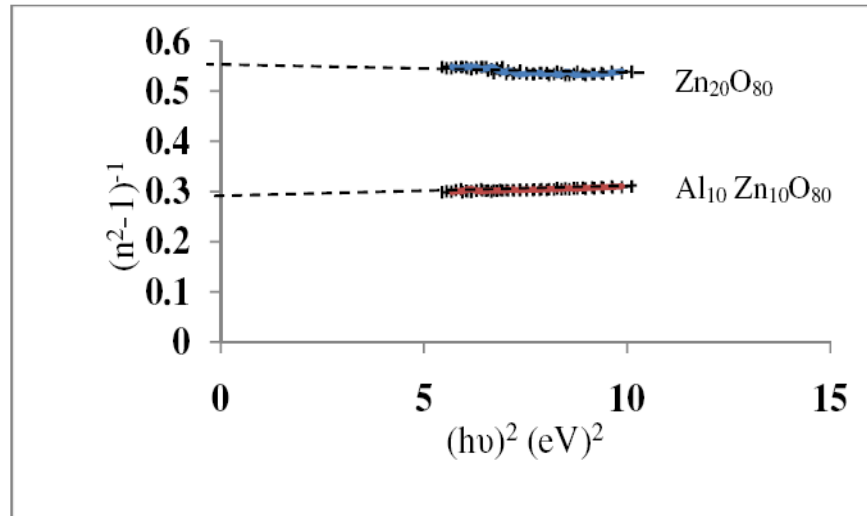


Fig. 5: Plot of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ for $Zn_{20}O_{80}$ and $Al_{10}Zn_{10}O_{80}$ thin films glasses

The values of the dispersion parameters and band gaps of the films are presented in table 1. It is clear that there was a blue shift in energy band gap after Al^{3+} doping (fig.3); this can be attributed to crystallites enhancement, hence exciton confinement effect which was contributed by Al^{3+} doping.

Table 1: Dispersion parameters and band gap energies of $Zn_{20}O_{80}$ and $Al_{10}Zn_{10}O_{80}$ thin films.

Sample	E_g	E_0 (eV)	E_d (eV)	M_{-1}	M_{-3} (eV) ²	n_s	ϵ_∞
$Zn_{20}O_{80}$	3.80	5.84	10.235	1.751	0.051	1.250	1.571
$Al_{10}Zn_{10}O_{80}$	3.60	6.00	20.746	3.460	0.096	1.135	1.289

The values of oscillator energy E_0 , optical moments M_{-1} , M_{-3} , and oscillator strength E_d also increased after Al³⁺ doping. The substantial increase in the oscillator strength E_d (more than two times), is usually associated with the evolution of the thin film microstructure to a more ordered phase [13]. However, the static refractive index n_s and the high energy dielectric ϵ_∞ constants were observed to decrease on Al³⁺ incorporation. Our observation that the oscillator energies $E_0 \approx 1.5 E_g$ for Zn₂₀O₈₀ and $E_0 \approx 1.7 E_g$ for Al₁₀Zn₁₀O₈₀ is in good agreement with $E_0 \approx 2 E_g$ [8- 9, 13- 15].

4. Conclusions

Glassy thin films of undoped ZnO and Al³⁺ doped ZnO were synthesized at room temperature using chemical bath deposition and analyzed to determine their optical dispersion parameters namely: oscillator strength, oscillator energy, optical spectra moments, static refractive index and high frequency dielectric constants. The films were observed to obey the single oscillator model and the computed values of oscillator parameters varied with Al³⁺ incorporation.

Acknowledgements

The authors wish to thank professor Obiajunwa of the accelerator unit, Centre for Energy research and Development (CERD), Ife, Nigeria, for RBS measurements. We also thank Mrs Tessy Eze of Engineering Materials Development Institute, Akure, for her technical assistance.

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