

The Effect of Annealing Temperature on Structural and Solid State Properties of Aluminum Zinc Oxide (AlZnO) Deposited by Chemical Bath Technique

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ABSTRACT

In this work, we studied the effect of annealing temperature on the structural and solid state properties of AlZnO thin films using Chemical bath deposition technique. The thin films grown was annealed at various temperatures of 100°C, 150°C to 200°C. The morphological and structural properties were studied using XRD and SEM, while the optical properties were studied using UV-VIS Spectroscopy from where the band gap, dielectric constant, refractive index, extinction coefficient, and optical conductivity were deduced from the theoretical equations. From the result, it is observed that there is effect of annealing temperature on these properties such that the grain size and x-ray characteristics depicted different characteristics at these various temperatures.

(Keywords: AlZnO, thin films, annealing temperature, chemical bath deposition, structural and solid state properties).

INTRODUCTION

In recent times, there has been interest and focus on the study of structural and optical properties of AlZnO thin film due to its response to modifications when it is subjected to annealing. Further work has also been carried out in order to ascertain the influence of deposition growth technique on the properties of this film (1). This is because of its applications in both microelectronics and photovoltaic cells (2) and as a filter to electromagnetic radiations coupled with the fact that its properties could easily be improved upon by doping and annealing which also results in tailoring the film to another area of application such as sensors.

This thin film material is a II-VI compound semiconductor with a hexagonal wurtzite crystal lattice structure (3). ZnO is also seen as a better replacement for Indium tin oxide widely used as a transparent conducting oxide TCO (4) because it is more abundant and nontoxic.

Zinc Oxide thin film is found to have a large band gap of about 3.33-3.37eV, It is one of the potential materials for being used as a TCO due to its good optical and electrical properties. Zinc Oxide (ZnO) thin films are an inexpensive n-type semiconductor having large and direct band gap of about 3.3 eV and is one of the most potential materials for used as a TCO because of its good electrical and optical properties, abundance in nature, [5, 6] and the ability to deposit these films at relatively low substrate temperatures [7].

Pure ZnO thin films are not stable against corrosive environments as adsorption of dioxygen in the films decreases the electrical conductivity and also modifies the surface morphology (8). These films become more stable by doping them with trivalent metal cations[9-11] especially with aluminum (12) Al doped ZnO is cheap, more abundant, non-toxic and has good stability in hydrogen plasma and above all its optical and electrical property can be improved or modified by controlling their doping concentrations [13], which is critical to achieving fictionalization and tunability of TCO-based devices. Therefore, it is useful to investigate the correlation between the optical properties of Al-doped ZnO films and the concentration of Al doping which enhances the band gap.

In such type of materials whose band gap is reasonable for use in optoelectronics, apart from the dependence of band gap on the width of the gap between valance band and conduction band, it also depends on the electronegativity of the

constituent atoms in the lattice of the crystal plays a role. It has also been observed that the microscopic inter-atomic spacing and the macroscopic differences of electronegativity of the component atoms [14].

While discussing the optical properties of materials, the refractive index plays also plays an important role in choosing the materials for the optical application purpose. The process of electronic polarization of constituent ions and the local field produced inside the optical materials are very much associated with the refractive index. For designing various optical materials especially optical windows, prisms, and optical fibers the refractive index plays an important role, and also various optical processes depend upon the value of refractive index. From the refractive index, various other optical parameters can be calculated like optical conductivity, real and imaginary parts of the complex dielectric constant which helps to design and frame new material devices.

Numerous techniques have already been used to deposit both doped and undoped ZnO thin films on different substrate including spray pyrolysis, organ metallic chemical vapor deposition [15], pulsed laser deposition, sputtering [16], and sol-gel process [17]. Among these, Chemical Bath Deposition, (CBD) is relatively new and a less investigated process credited with several advantages, such as deposition of high purity, homogeneous, large-area films at relatively low temperature [18] and because based on the fact this material can be amenable to optoelectronics application, we have opted to doped ZnO with Al and anneal it in order to ascertain how the modification of its properties based on the Al dopant and annealing could affect its properties for the application and as such we used the CBD technique which seems and proves to be simpler, reproducible and inexpensive as compared to other growth techniques.

EXPERIMENTAL PROCEDURE

ZnO thin films prepared by CBD method is based on the heating of alkaline bath of zinc salt containing the substrates immersed in it. 0.1M of zinc sulphate was used as a source of zinc, to make the solution alkaline, aqueous ammonia solution was added with constant stirring. Firstly, the solution became milky-turbid due to the formation of zinc hydroxide $Zn(OH)_2$. Further

addition of excess ammonia dissolved the turbidity and made the solution clear and transparent. The pH value of the resultant solution was ~11.0.

The substrates were immersed in the bath at room temperature and the bath was heated at a temperature of 343K for 2 hours, heterogeneous reaction occurred and the deposition of ZnO took place on the substrates. The ZnO coated substrates were removed from the bath washed with distilled water, dried in air and preserved in an air-tight container. These procedure leads to deposition on undoped ZnO on the glass substrate. To deposit Aluminum doped ZnO (AZnO) thin film, 0.3M of Al was added to the starting material.

A total of four thin films were fabricated. One of these thin films was kept as deposited whereas the other three were annealed at 100°C, 150°C, and 200°C respectively.[19] The crystallographic and morphological structures for both as-deposited and annealed AlZnO thin films were analyzed using X-ray diffraction (XRD) and Scanning Electron Microscope (SEM), respectively.

The optical characteristic within the ultraviolet and near infrared region of electromagnetic wave spectra was analyzed using UV-VIS spectroscopy to determine the transmittance from which other optical parameters such as band gap, refractive index, extinction coefficient, optical conductivity and dielectric constants were computed [20, 21, 22].

THEORETICAL DEDUCTIONS

The solid state properties were deduced from the related equations using the parameters obtained from the experimental values.

Absorption Coefficient

Absorption coefficient (α) is the rate of decrease (or attenuation) of the radiation intensity when it passes through a thin films sample of thickness (α). The absorption coefficient α was analyzed using the following expression for optical absorption of semiconductors [23, 24].

$$\alpha = \frac{2.3026A}{t} \quad (1)$$

Where, A= Absorbance, t = thickness.

The absorption coefficient α is related to the incident photon energy $h\nu$ as:

$$\alpha = \frac{k(h\nu - E_g)^{\frac{n}{2}}}{h\nu} \quad (2)$$

Where K is a constant, E_g is the optical band gap, and when n is a unity, the material is direct band gap material such as in ZnO [25].

Extinction Coefficient

Extinction coefficient (K) was calculated from the absorption coefficient using the classical relation [24].

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

Where α = Absorption coefficient, λ = Wavelength.

Optical Band Gap (E_g)

Near the absorption edge, absorption coefficient (α) is related to band gap (E_g). The optical bandgap (E_g) was determined from the formula:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (4)$$

Equation 4 can be written as:

$$E_g = h\nu - \frac{(\alpha h\nu)^{1/n}}{A} \quad (5)$$

Where $h\nu$ is the incident photon energy, A is a constant, which are characteristics of the crystalline and amorphous semiconductor material, the exponent n depends on the type of transition; n = 1/2 and 2 for direct and indirect transition, respectively [26].

Refractive Index

This is given by the formula below:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (6)$$

Where R = reflectance, n = refractive index and k = extinction coefficient

For insulators, Semiconductors and materials with weak absorption as $k^2 \ll (n-1)^2$

i.e., k is very small. Thus eqn (22) reduces to:

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (7)$$

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (8)$$

Optical Conductivity

The optical conductivity (σ_{opt}) of the AlZnO thin films can be calculated using the following relation.

$$\sigma_{opt} = \frac{\alpha n c}{4\pi}$$

or

$$\sigma_{opt} = \frac{1}{e\mu_{opt} N_{opt}} \cdot [27, 28] \quad (9)$$

Where n is refractive index, c is speed of light and α is the absorption coefficient.

Dielectric Constant (Real and Imaginary)

The fundamental electron excitation spectrum of the AlZnO thin films were described using the frequency dependence of the complex dielectric constant. The dielectric constant is a property of the material and determines the movement of electromagnetic radiation through it. The real and imaginary dielectric constants were estimated using the formulas below respectively.

$$\epsilon_r = n^2 - k^2 \quad (10)$$

$$\epsilon_i = 2nk \quad (11)$$

Where n is the refractive index and k is the extinction coefficient. Both n and k are functions of wavelength, λ of light.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

The surface properties are very important and play a crucial role towards different physical properties of thin films. So to study the surface morphology of all AlZnO thin films, scanning electron microscopy (SEM) was done and the corresponding SEM micrographs are shown in Figure 1 (a-c). The SEM micrograph of as deposited thin film (Figure 1a) reveals good smooth surface morphology as the film possesses uniform distribution of particles with no particulates on the surface. The shape of the particles on the surface of as deposited thin film is not visible at this magnification.

Figure 1(b) shows the SEM micrograph of AlZnO thin film and it is evident that with the increase of annealing temperature, the surface morphology of this thin film has been affected as the surface has become rough as compare to previous thin film , it is observed from the micrograph that the size of the grains become denser and larger as it is annealed at higher temperatures, This could be attributed to the effects of evaporation of absorbed water and reorganization of the grain.

On further increase in temperature up to 150°C for Figure 1(c), the effect of annealing temperature has appeared to be very interesting as Some flower like structures have been observed on the surface of this thin film. These flowers like structures are not well separated from one another although some boundaries can be clearly seen in the Figure 1(c).

Finally, for Figure 1(d) thin film annealed at maximum temperature of 200°C, these flower like structures are very well separated from each other. Each flower like structure looks as a nucleation center for growth of structures that can be seen at the center of these flowers.

These patterns in Figure 2 (a-c) reveal that all films are polycrystalline in nature having hexagonal wurtzite crystal structures. “The increase in the intensities of the peaks as annealing temperature increases is an indication that the crystallinity of the films has improved due to annealing (17).

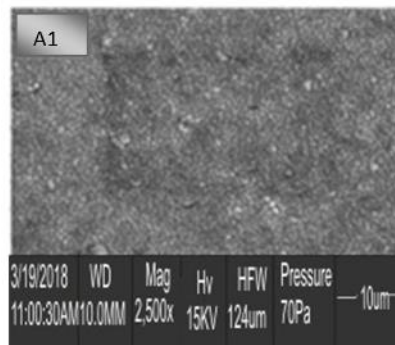


Figure 1A: SEM Image of pure AlZnO.

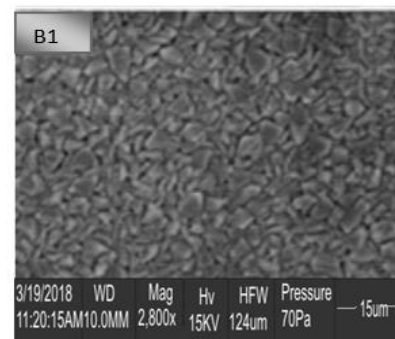


Figure 1B: SEM Image of AlZnO annealed @ 100°C.

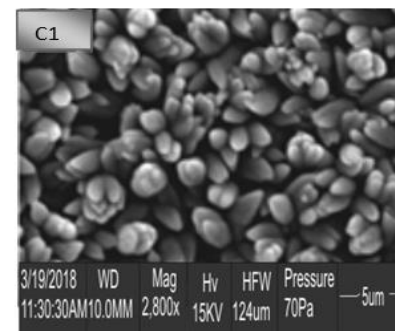


Figure 1C: SEM Image of AlZnO annealed at 150°C.

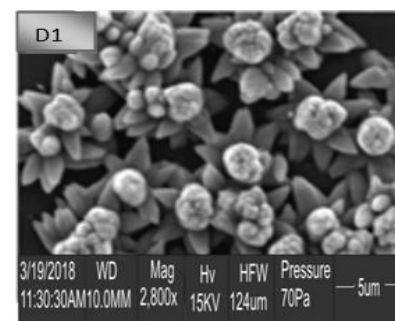


Figure 1D: SEM Image of AlZnO annealed @ 200°C.

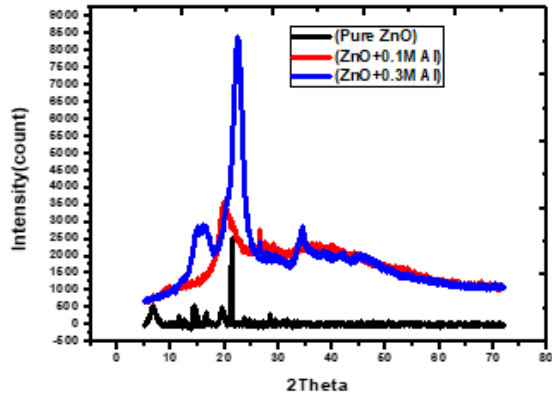


Figure 2A: XRD Pattern of As-Deposited AlZnO.

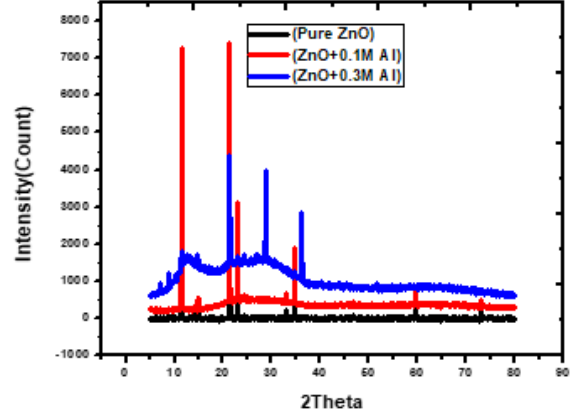


Figure 2D: XRD Pattern of ZnO Annealed at 200 °C.

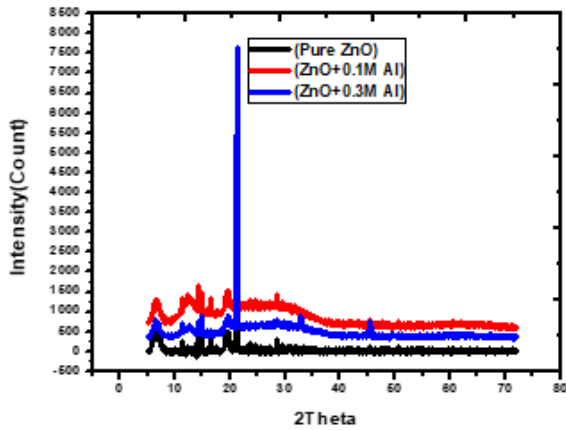


Figure 2B: XRD Pattern of AlZnO Annealed at 100 °C.

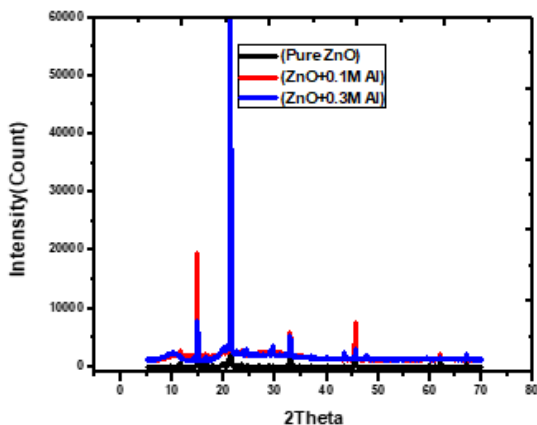


Figure 2C: XRD Pattern of AlZnO Annealed at 150 °C.

Optical Band Gap

Figure 3 shows the plot of $(\alpha h\nu)^2$ vs $h\nu$ which reveals that the electronic energy band gap AlZnO is dependent on annealing temperatures, it was also found that absorption edges shift toward lower wavelength value by increasing post-heating temperature. It means that the optical band gap of AlZnO film was decreased by post annealing temperature. The value is within the range of (3.5-3.8eV). The observed band gaps are within the range of values reported in the Literatures (25, 29).

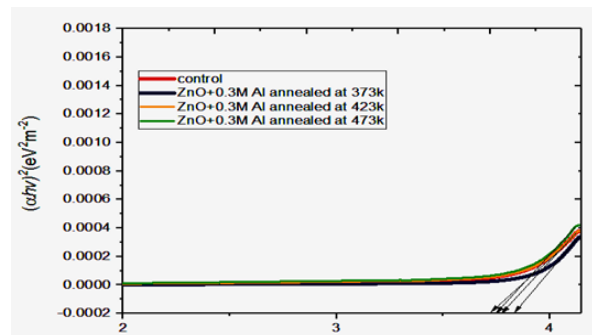


Figure 3: AlZnO Graph of $(\alpha h\nu)^2$ as a Function of Photon Energy.

Refractive Index

Figure 4 shows that the indexes of refraction were from 1.40 to 2.40 for all the samples. We observed from the plot that the value of refractive index tends to decrease as photon energy increases for all samples until 3.4eV which is the energy corresponding to energy band gap and increases gradually from 3.5eV. We also observed from the plot that the refractive index increased with a corresponding increase in annealing temperature. The behavior is not in trend as the highest index of refraction occurs in 100°C.

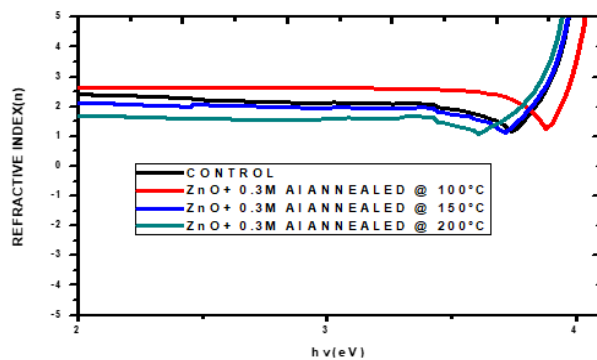


Figure 4: Refractive Index (n) against Photon Energy for AlZnO.

Extinction Coefficient, k

It is observed from Figure 5, that (k) decreased up to the region of the fundamental absorption that is the range of photon energies at which the energy band gap occurred and then increased afterward. However, the values of k for un-annealed samples are higher compared to that of the annealed samples. Also seen is a gradual increase in k values after band gap value towards the higher photon energy value and the positive value shows that the material is strongly absorbing and that will be ascribed to the surface smoothness of the sample and uniformity of the solution.

Optical Conductivity

It is observed from Figure 6 that the optical conductivity is high within the infra-red region and increases with increase in annealing temperature.

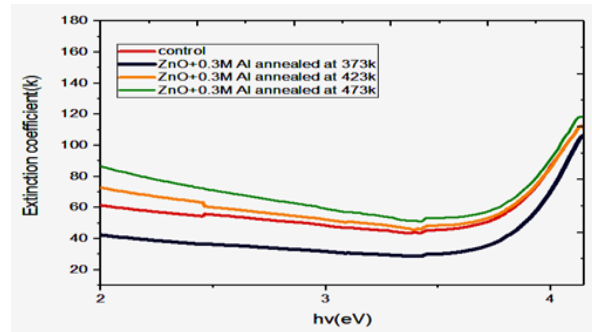


Figure 5: Extinction Coefficient (k) against hv for AlZnO.

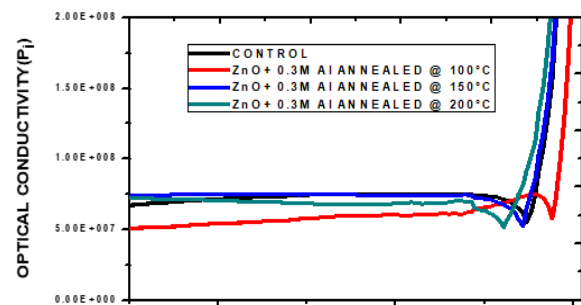


Figure 6: Optical Conductivity against Photon Energy of AlZnO for Various Annealed Temperatures.

The plots in Figure 7 (A & B) indicates, that the real dielectric constant, ϵ_r for all deposited AlZnO thin films ranges from -13000 to -2000 which increases as the annealing temperature increases. While imaginary dielectric constant (ϵ_i) for all deposited AlZnO thin films ranges from 350 to 400.

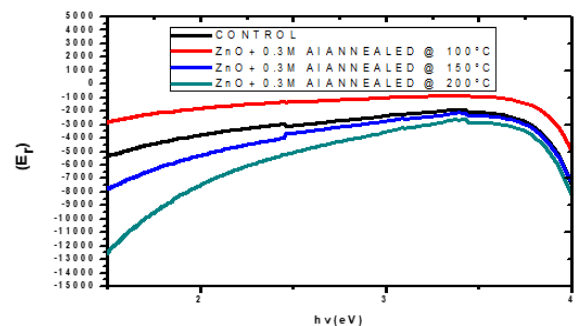


Figure 7A: Real Dielectric Constant against hv for ZnO Doped with 0.3M of Al.

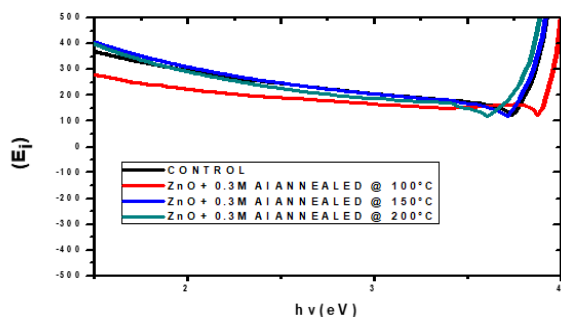


Figure 7B: Imaginary Dielectric Constant against $h\nu$ for ZnO Doped with 0.3M of Al.

Generally, the plot reveals that all the samples have low real dielectric constants and higher imaginary dielectric constant and Materials that have high value of this constant allows light to pass through it slowly.

CONCLUSION

The structures of the AlZnO thin films studied reveals that XRD patterns show peaks increase with an increase in temperature during heat treatment. Different reflection peaks were seen in all AlZnO thin films with other peaks appearing after annealing. This is the proofs that annealing has a profound effect on the structural properties of the films [30] and also it could be noticed that some of the solid-state properties were modified by aluminum doping and annealing.

Generally, wide energy band gap shown by these films, suggest that these films could be employed in solar cell architecture as window layer. This proofs that annealing effect have a superficial effect on the absorbing properties of the deposited AlZnO films. The energy band gaps of these films fall within the range of (3.5-3.9eV). This decrease in band gap when annealing temperature increases shows that annealing enhances the band gap and the wide band gap exhibited by these films, suggest that these films are good materials for application in laser diode and photovoltaic applications. The index of refraction and extinction coefficient was also found to vary with post annealing temperature. In general, the deposited film is a possible material that can be used for optoelectronics and solar harvesting application.

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