Chapter 2

The Effect of Annealing, Doping on the Properties and Functionality of Zinc Oxide Thin Film; Review

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Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/intechopen.79018

Abstract

The review of the effect of annealing and doping zinc oxide thin films on both the structural and optical properties has been carried out for different growth techniques such as sol–gel growth technique. The structural and optical properties were carried out using thin films were characterized SEM, XRD while TE and TM guided mode spectra, UV–VIS–NIR (HR4000Ocean Optics) and UV–Visible spectrometry were used accordingly respectively. From the results, it was clearly observed the both the morphological and the crystal characteristics structural characteristic, although increase in the percent of doping element affected it as the diffraction peak was shifts slightly to a lower angle side with report that crystal structure of the film deteriorate at a higher doping concentration of doping element as it decreases the c-lattice. There was also adjustment on the band gap of the material when it was annealed at various temperatures and also when the doping concentration was varied. The film exhibited lower absorbance, high transmittance depend on the regions of electromagnetic wave spectra.

Keywords: zinc oxide film, sol–gel deposition, chemical bath deposition doping, annealing, structural and optical properties, morphology, characteristics, analysis, absorbance, transmittance, band gap

1. Introduction

The aim of this review work is to overview the rapid progress of thin film techniques to grow ZnO based thin film which has been on course for long and to view how doping and annealing using different growth techniques affects its characteristics and functionality.

Zinc Oxide, ZnO thin film is one of the most oxide based thin film materials of the II-VI semiconductors are being studied since early twentieth century with great interest by non-scientists

world-wide [1]. Now due to its current applicability to several novel devices**,** electronics, opto-electronics there has been a renewed attention are being given to this material thin film [2, 3].

At various point in time, conferences had been held and the proceedings published exclusively for ZnO thin film in some places such as Singapore and Changchan in China during 2005, 2009 and 2005 respectively based on exploring the efficacy and potentiality on the applicability of the thin film in order to create awareness on the feasibility of commercial application of the thin film for feature devices. Yet it seems as if the realm of the novel devices from this wonderful and unique oxide based thin film material is yet to be actualized in full [4]. With a direct band gap of 3.2 eV and large excitation energy of 60 meV at room temperature ZnO thin film just like GaN is a good candidate for blue and ultraviolet-optical devices [5]. Though it has more excitation energy and wider band gap than GnN, it can be grown into single crystal on the substrates with its good broad chemistry which leads to opportunities for wet chemical etching, low power threshold for optical pumping, radiation hardness and biocompatibility, thermal stabilities and environmental friendly nature [6]. Crystallographically, ZnO thin film has a hexagonal closed packed structure, wurtizite type with the zinc and oxygen ionic plane stacked alternatively along the principal axis of the symmetry which made to it have an excellent piezoelectric and optical properties [7–9]. The flexibility of the its heterostructures has been found to lead to expanded possibility of its device functionalities to various kind of application apart from solar energy devices. Uniquely apart from its easy realization of bipolar based devices due to doping symmetry issue which characterizes other II-IV semiconductors that can be readily doped n-type, it has been found very difficult to reproduce the ZnO doped p-type semiconductor because of lack of dopants having shallow acceptor level as a result of low dopant stability [10]. The dopants also affects in a strong term the microstructural, electrical and optical characteristics of the thin film [11, 12]. Glaringly, it has been ascertained the doping an annealing optimizes the solid state and optical characteristics of ZnO thin film [13–18]. It has been reported that doping do not only affect the optical properties of ZnO thin film but also the physical properties [11, 19].

In this paper we wish to review how doping and annealing of zinc oxide thin film affects the structural and optical characteristics and how it restructures the properties for utilization in optoelectronic and solar energy application.

2. Materials and methods

Various methods has been used to grow ZnO thin film at different time and places such as chemical bath deposition, sol–gel growth techniques, radio-frequency magnetron sputtering and chemical vapor deposition under low vacuum condition, etc. In the case of CBD, different complex agents such as ammonia, hydrazine, ethanolamine, methylamine, triethanolamine, etc. has been used to deposit the thin film both at room temperature and at annealed temperature ranging from 150 to 400°C [19–21] while spray pyrolysis using aqueous methanolic solution zinc acetate as spraying solution has been used to develop the thin film apart from the use of ultrasonic spray pyrolysis technique that was carried out at 200 to 500°C by many researchers [3, 22]. Apart from atomic layer deposition technique that has been reported a good candidate for the growth of high performance n-type growth of ZnO at low temperature

sol–gel technique has not been has been employed using $Zn(CH_3COO)_2.2H_2O$ as a starting material to prepare an acetone gas sensor for use for the growth of the thin film temperature ranging between 700 and 800°C. ZnO thin film has been doped with different elements using different growth techniques such as Sol–gel, Magnetron sputtering, CBD, Spray CVD etc. [23–27]. The morphological structures for both as-deposited, annealed and doped ZnO based thin films were analyzed using SEM of different models such as Hitachi-S4500, JEOL6390-LV respectively; and the same for the optical characterization, different models of spectrometers such as TE and TM guided mode spectra, UV–VIS–NIR (HR4000Ocean Optics) and UV–visible spectrometry were used accordingly respectively.

Other optical parameters such band gap, extinction coefficient and optical conductivity were computed using the relations [28, 29].

$$(h\alpha v)^2 = C\left[h\upsilon - E_g\right] \tag{1}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{2}$$

$$\sigma_o = \alpha nc\,\varepsilon_o \tag{3}$$

where the α is absorption coefficient that is dependent on the photon energy and c and n are the velocity of light and the refractive index of the film respectively.

3. Results/discussion

3.1. Morphological analysis

The binding energy of the ZnO thin film deposited by single source chemical vapor deposition technique was analyzed with the region XPS spectra and was found to be about 532.2 eV which was attributed to the effect of zinc hydroxide on the surface of the film [30]. Similarly, the value obtained for the same thin film prepared by chemical spray pyrolysis on silicon using wide scan XPS on the deposited thin film depicted high value 530.19 and 531.82 eV respectively due to O—Zn bond and O—H bond absorbed water molecule [22]. Contrarily the theoretical excitation energy proposed for the same thin film in the literature was just 60 meV at room temperature. The morphological characterization was carried out by SEM. The observation as in **Figures 1** and **2** indicated that the surface and cross-section morphologies of pure ZnO thin films has smooth surface and dense polycrystalline microstructure in the form of small grain with increase in particle size at high annealing temperature while in the case of **Figure 3**, the Te-doped SEM micrographs it was found that the grains were oriented and larger than those observed in pure ZnO. However, in Cu-doped ZnO thin film the morphology depicted a decrease in grain size with percentage increase in copper concentration with annealing affected the microstructural properties while in case of aluminum doped ZnO thin film it was seen that the increase in Al concentration alone led to a significant increase in improvement of the crystal compactness of the structure as in **Figure 4**.

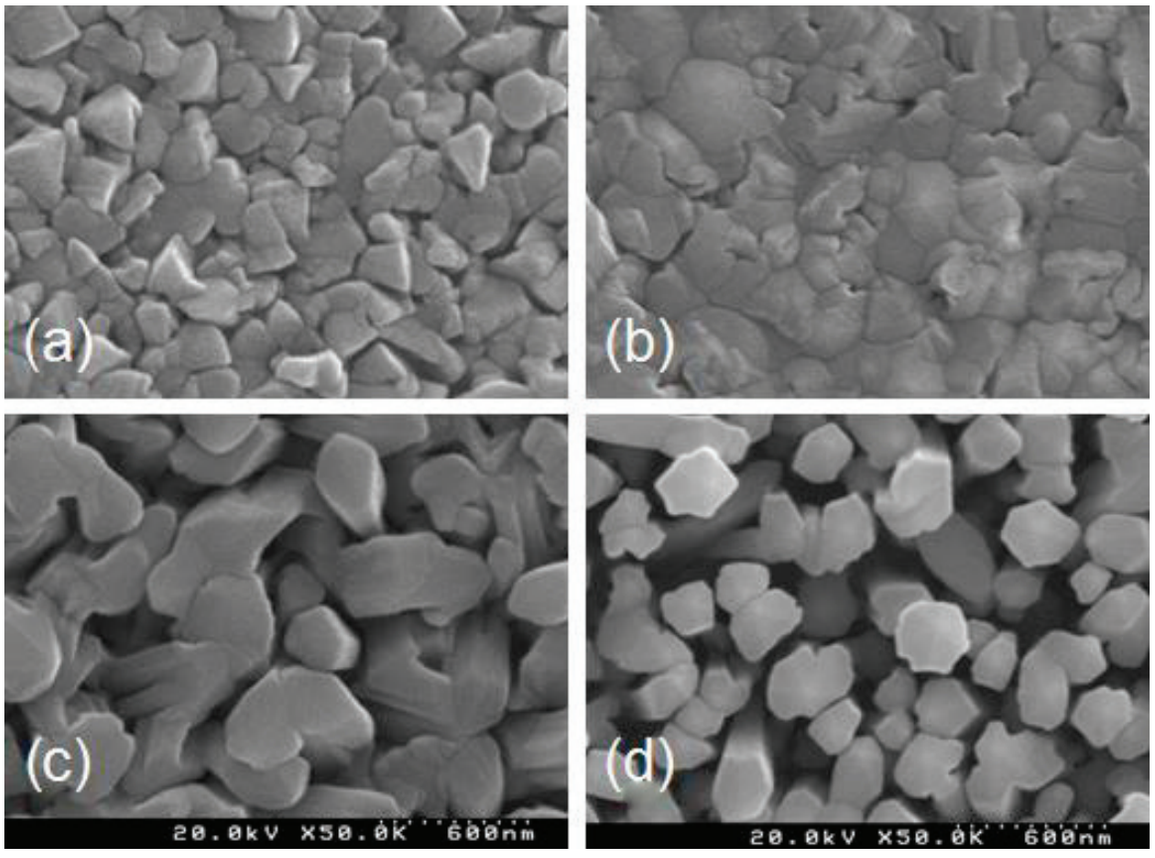

Figure 1. SEM surface morphology [a–d] of pure ZnO thin film annealed at temperatures of 100, 200, 300 and 400°C respectively.

3.2. Structural analysis

The XRD analysis allows us to determine the crystal orientation of both the as-deposited, doped and annealed ZnO thin film on glass substrates. The diffraction patterns of the samples for all these mentioned cases are depicted in **Figures 5–9** respectively and from the analysis, it was seen that as-deposited ZnO thin film had common intense peaks irrespective of time of growth and substrate temperatures occurring within $2\theta = 32°$ and 36° along the following orientations

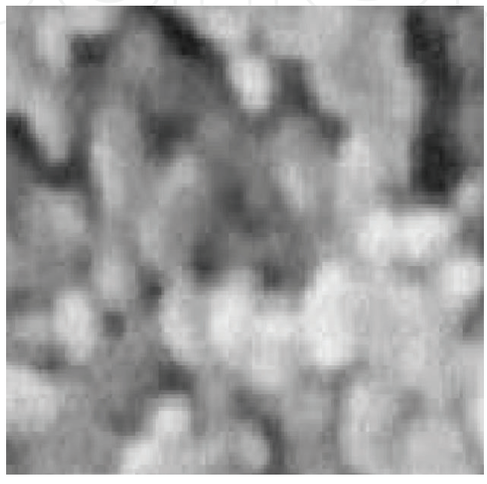

Figure 2. SEM morphological structure of undoped ZnO thin film at magnification ×50,000.

http://dx.doi.org/10.5772/intechopen.79018

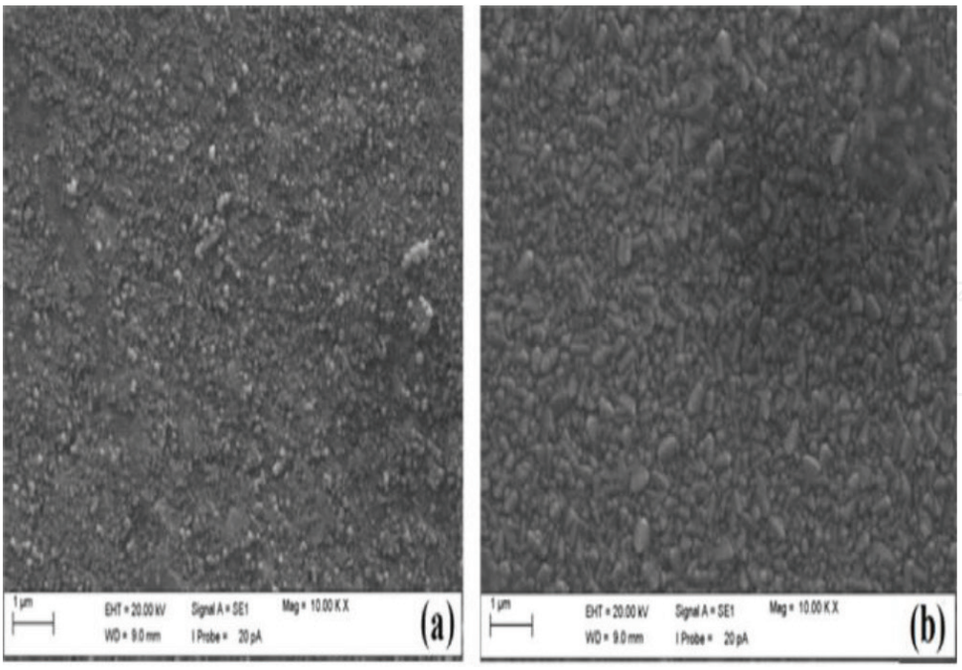

Figure 3. SEM morphological structures of as deposited and Tellurium doped ZnO thin film (a and b).

(100), (002) and (101) as in **Figures 5** and **6**. In the case of Cu-doped and boron doped ZnO thin film, intense peaks were observed at (100), (002),(101 and (102) respectively all occurring within 30° and 40° with increase in the intensity of the peak as annealing temperature increases as in

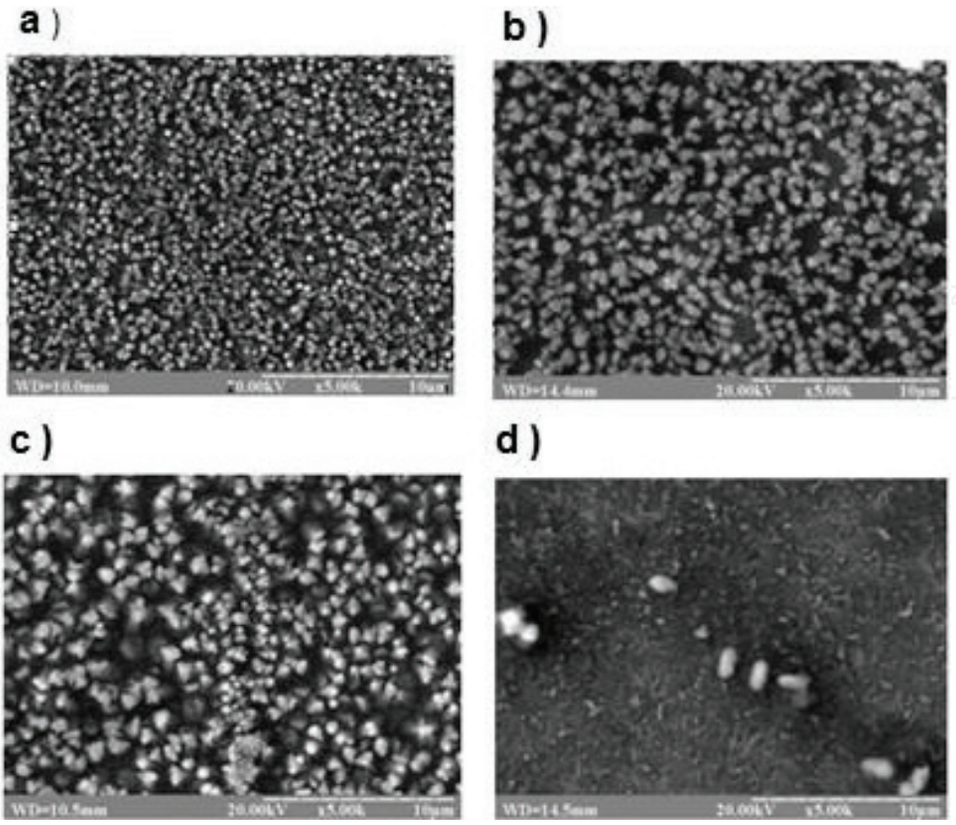

Figure 4. SEM morphological structure of Cu-doped ZnO thin film [a–d] as deposited and annealed at temperature; 500, 700 and 850°C.

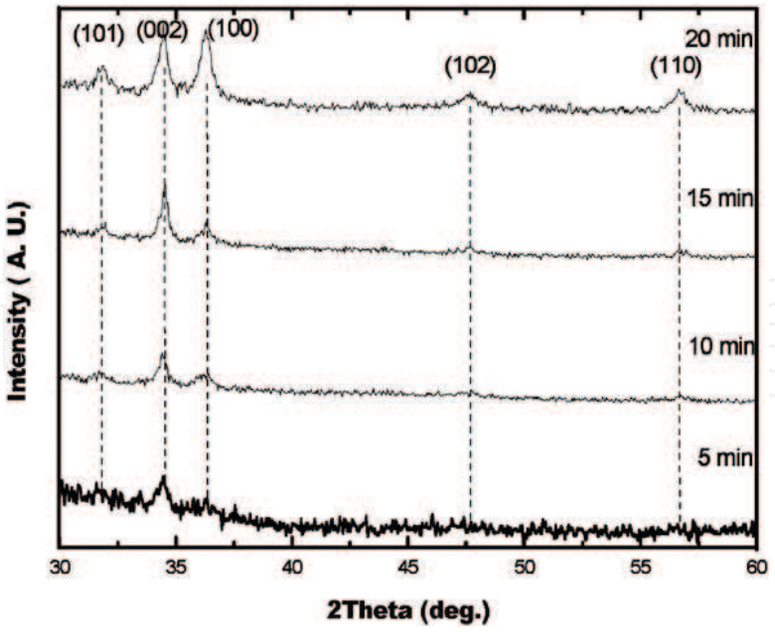

Figure 5. XRD spectra for pure and [1, 3, 5] % Al doped ZnO thin films.

Figure 7. The XRD for boron doped ZnO as in **Figure 7** exhibited defined intense peaks along (100),(002), (110) (103), (200) and (112) within 32° to 37° and 48° and 67° respectively while for Al-doped, intense peaks were identified along (100), (002) and (101) at 2θ = 36.24, 32.37 and 36.24° respectively. Generally it was seen that irrespective of annealing growth technique and doping not withstanding doping element used, ZnO has high diffraction peaks elaborated at (100) and (002) in all cases This observation indicated that ZnO thin film is strongly c-axis oriented with wurtizite structural characteristic, although increase in the percent of doping element affects and often shifts the diffraction peak slightly to a lower angle side with report that crystal structure of the film deteriorate at a higher doping concentration of doping element as it decreases the c-lattice [10, 13, 25].

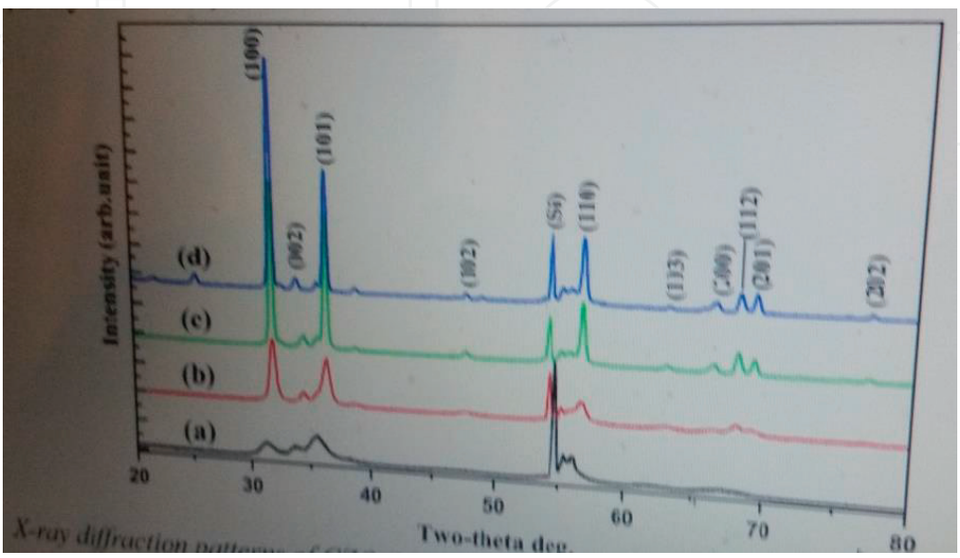

Figure 6. XRD spectra for pure ZnO thin film for different deposition time.

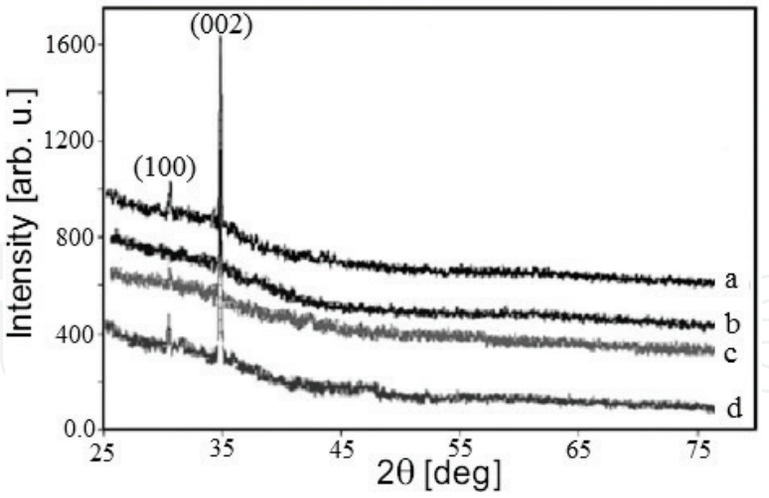

Figure 7. XRD spectra of pure and Cu-doped ZnO thin film annealed at temperatures; 500, 700 and 850°C.

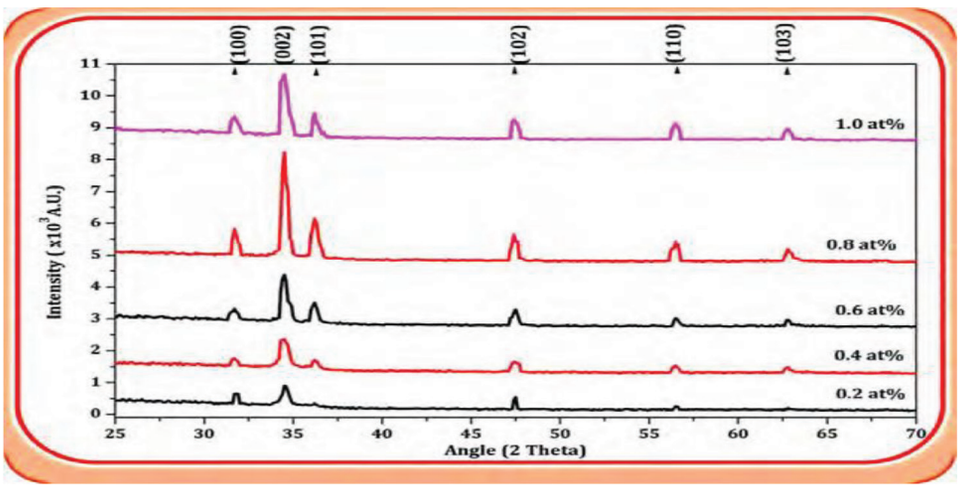

Figure 8. XRD spectra for various percentage boron doped ZnO thin film.

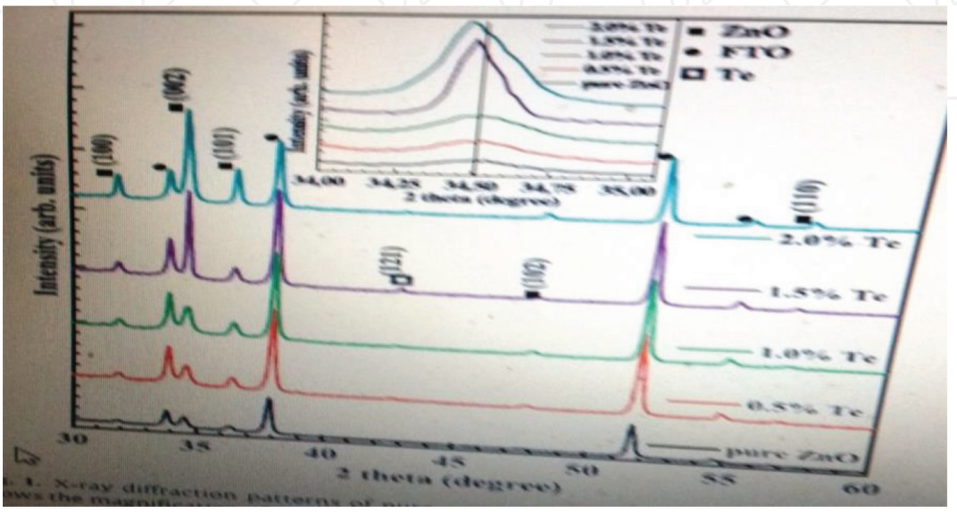

Figure 9. XRD spectra of pure and varying percentage tellurium doped ZnO thin film.

3.3. Analysis of the energy band gap

The band gap of ZnO thin film as recorded in the all the experiment for both as deposited, annealed and doped was based on Tauc model which involved a plot of a curve of $(\alpha h\upsilon)^2$ as function of photon energy, $h\upsilon$ (eV) [22]. In the plot, the band gap is obtained by extrapolating the straight line portion of the curve/tangential line to the photon energy axis from the extrapolation as in **Figure 10**, it was observed that the band gap for pure an annealed ZnO shifts/narrows from

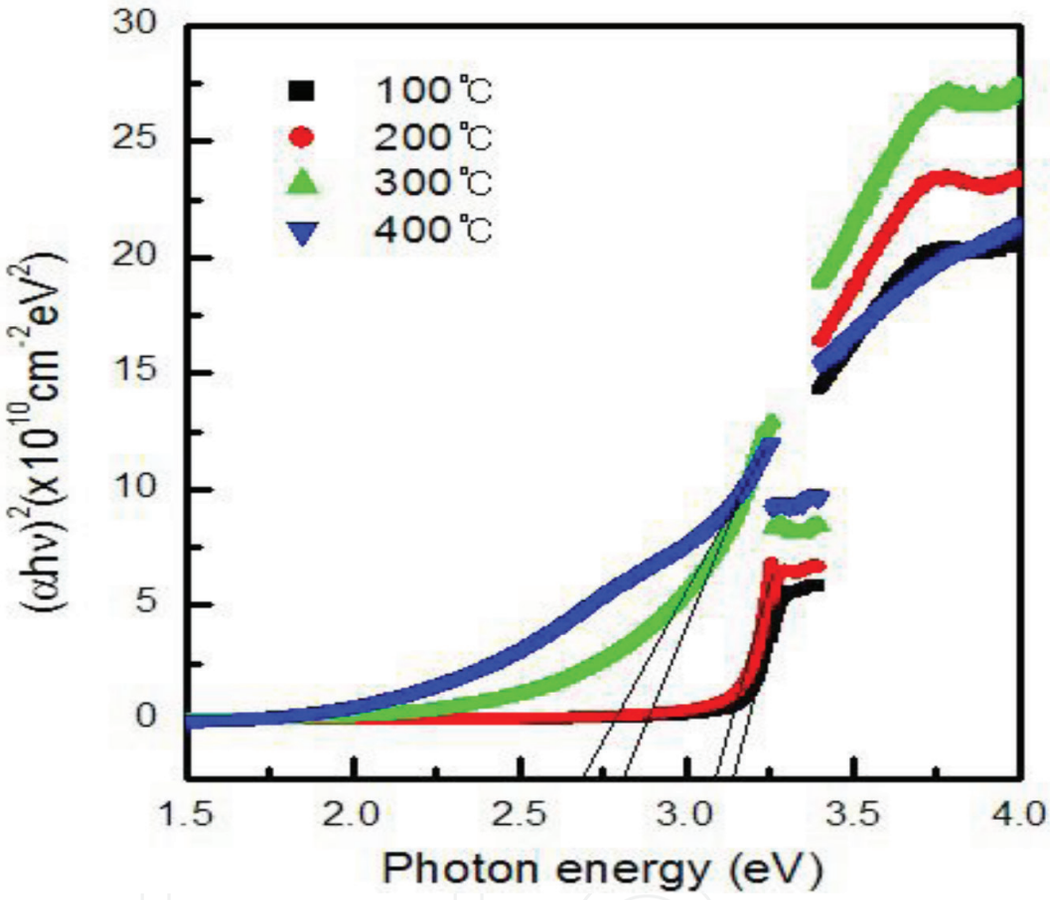

Figure 10. Graph of $(\alpha h\upsilon)^2$ as a function $h\upsilon$ for pure ZnO thin film grown under different temperature.

3.13 eV at 100°C to 3.09 eV at 200°C and finally to 2.69 eV at 400°C respectively. This is in accordance with Ayouchi report in his work [22]. Form the Tellurium doped ZnO thin film, using the same Tauc model, it was noted that the undoped film has its band gap as 3.18 eV the percentage doping concentration of Te increased the energy band gap up to maximum of 3.42 eV for 1.5% of tellurium doping concentration. This was as a result of transition energy degeneracy associated with semiconductor owing to the partially filled conduction band [30, 31, 32–34].

4. Absorbance/transmittance

The spectral absorbance of pure thin film deposited at different temperature as in **Figure 11** was found to be decreasing in slope slowly with a sharp sink observed within 779 nm after which there was decrease in the value of the absorbance the red region and infra-red region of electromagnetic wave spectrum.

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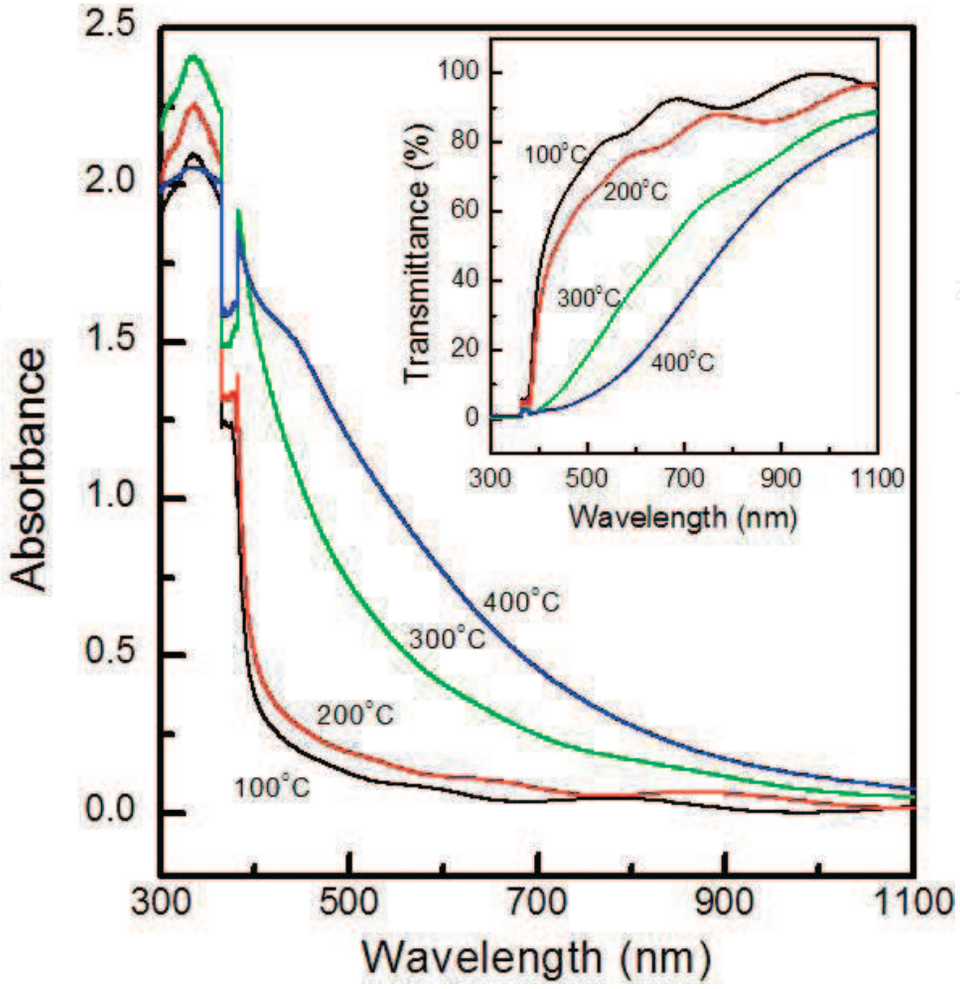

Figure 11. Spectral absorbance of pure ZnO thin film grown under different temperature.

The transmittance as observed in **Figures 11–13** for both pure annealed and doped ZnO thin films occurred within 600–1100 nm. From the report of ZnO doped with nitrogen had its transmittance increased between 395 and 590 nm and thereby remained constant within 80–90% around the infrared region [800–200 nm] which collaborated the results in the figures mentioned [27, 28].

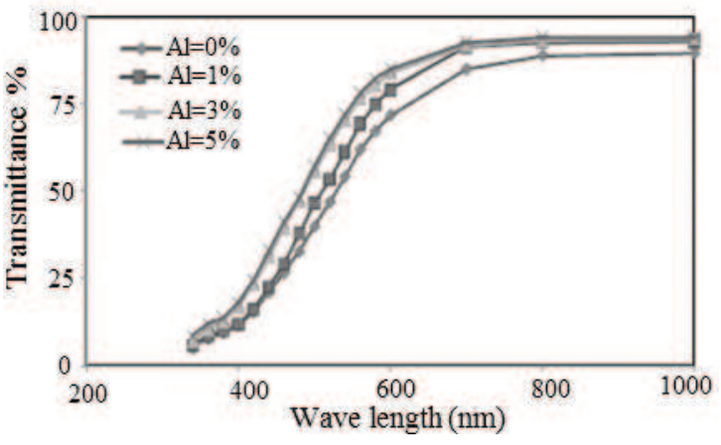

Figure 12. Percentage transmittance of ZnO dope with % aluminum.

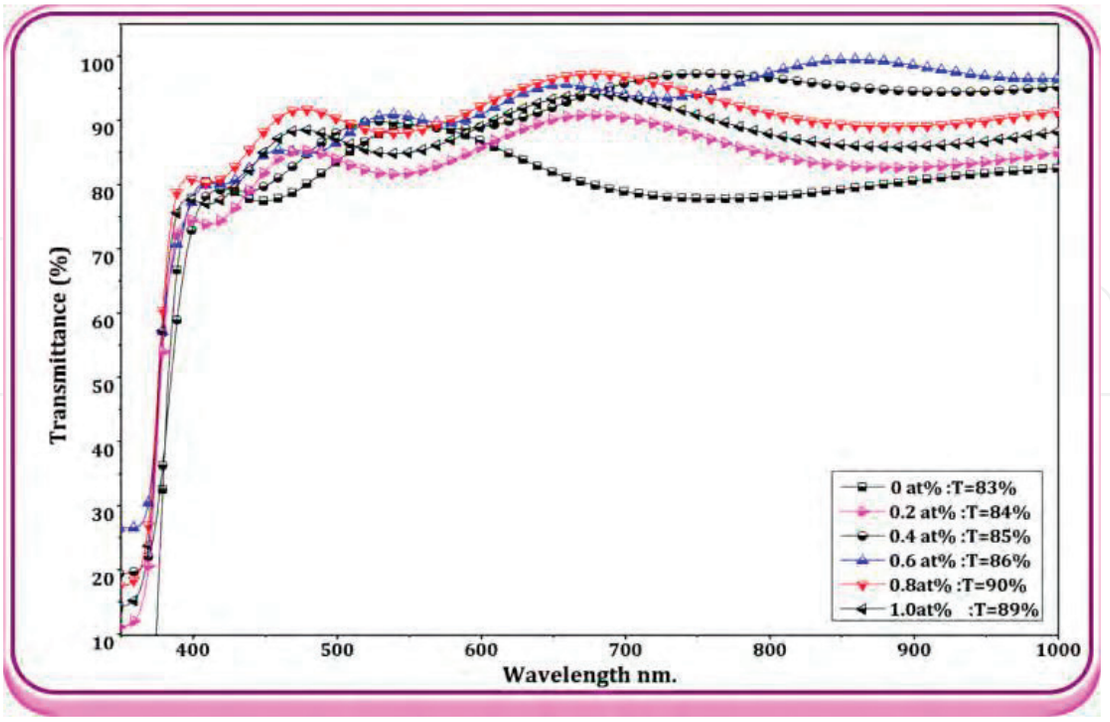

Figure 13. Percentage transmittance of ZnO doped with different % of boron.

5. Conclusion

It has been generally observed that ZnO based thin is very flexible so that it can adapted for some useful applications since the characteristics and properties can easily be modified by doping and annealing. From this review, it was noted that at low temperature, the morphology of ZnO thin film appeared to be smooth as a result of randomly oriented fine-grained polycrystals, but at higher temperature, the smoothness of the morphology become more pronounced with preferred c-axis orientation. Conversely, for ZnO doped with different elements, the grain size in SEM images increased with increase in the percentage concentration of the dopants which is an indication that the dopants influences the physical properties of the film which is invariably enhanced by the annealing. The surface morphology was found generally to be good with the stoichiometric formation of ZnO nanocrystals shape which demonstrates good aggregation of the particles and was suggested to have been originated from the large specific surface area and high surface energy as observed from the structural analysis.. From the XRD analysis in all the cases, ZnO thin film and its doped counterpart annealed at various temperatures depicted high and pronounced intensity at (101), (002) and (100) respectively according to [35, 36] with an increase in peak intensity as annealing temperature is increased in all the cases respectively irrespective of the growth technique and the dopant used during the growth of the film. Optically the spectral absorbance is seen to have high value within the visible widow where the percentage transmittance appeared to have lower value. On the other hand, the transmittance has a high percentage transmittance within near infra-red and infra-red region of electromagnetic wave spectrum. This result then presents ZnO based thin films as good candidate for UV filter and good infra-red transmitter and the thin film being a well-known direct band gap thin film with average band gap

of 3.31 eV. From the results it was obviously observed that for both sol–gel and other growth techniques analyzed in this work, there is not much deviation from the values of the band gap. This obviously goes ahead to suggest that ZnO based thin films irrespective of growth technique has a good range of band gap characteristic that made it good for application in optoelectronics, it could also be used as visibly transparent and heating films for use in a cold climate selective windows to transmit only visible and infra-red radiation into buildings while shutting off UV radiation. This will lead to warm indoor temperature in buildings which have their windows coated with such oxide based thin films. The observed wonderful features and tremendous opportunities in ZnO-based heterostructures make it unique and promising in oxide electronics based thin film and has led to new quantum functionalities in optoelectronic devices and electronic applications with lower energy consumption and high performance.

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