Original Research Article

Morphological and optical characteristics of ZnO and F:ZnO thin films by sol-gel spin coating technique

ABSTRACT

The increase in the application of transparent conducting oxides (TCOs) thin films has led to continuous demand for improved quality films for solid state devices. Indium tin oxide (ITO) which is mostly used as TCO is reportedly scarce, thus making it more expensive. This paper investigates physical characteristics and effect of temperature on sol-gel synthesized zinc oxide (ZnO) and fluorine doped zinc oxide (F: ZnO). Samples of ZnO and F: ZnO thin films were prepared by sol-gel spin coating technique using zinc acetate dehydrate as precursor, methanol as solvent, monoethanolamine as stabilizer and ammonium fluoride as dopant at deposition speed of 4000 r.p.m for 30 seconds and later annealed at temperatures ranged from 100 ^{o}C to 400 ^{o}C. The morphological and optical characteristics of prepared thin films were characterized using Scanning Electron Microscopy (SEM) and UV- Visible Spectroscopy respectively. The SEM images of the films showed good homogeneity with distinct grain size ranged from 10.31 to 11.97 nm for ZnO and 7.90 to 17.53 nm for F: ZnO. The average transmission in the visible range (300-1100 nm) for ZnO and F: ZnO thin films were greater than 80% and 70% respectively. The energy band gap increased with temperature ranged from 3.80 to 4.05 eV for ZnO and 3.76 to 3.90 eV for F: ZnO. There is a change in physical characteristics of ZnO and F: ZnO as the temperature varies. The obtained results from this study make ZnO and F: ZnO thin films suitable for solar cell and opto-electronic applications.

Keywords: Zinc oxide, F:ZnO, TCO, sol-gel, spin coating, annealing temperature, optical properties

1. INTRODUCTION

ZnO films are n-type wide-gap semiconductors with optical transparency in the visible region and several researchers have studied it extensively due to its interesting physical and chemical properties.

Zinc oxide (ZnO) a class of materials called transparent conducting oxide which is relatively less expensive, abundant in nature and non-toxic compared to other TCO such as indium oxide, cadium oxide and Tin oxide e.t.c.

ZnO is a II-VI group compound semiconductor with wide-gap semiconductors (3.37eV) and a large excitonic binding energy of 60meV [1]. It is used in UV-light emitting diodes, transparent electrodes, window layers, photovoltaic cells, varistors and also in the fabrication of hydrogenated amorphous silicon solar cell with better stability in hydrogen plasma when compared with that of indium oxide [2].

The properties of ZnO films can be further improved by doping and annealing. Doping with halogen (fluorine) a group VII element asides from the commonly group III elements such as gallium, boron and aluminium, fluorine act as dopants in ZnO thin films by anion substitution replacing the oxygen [3] and does not introduce significant perturbation into the conduction band due to the size compatibility of the oxygen and fluorine atoms.

However, there are numerous ZnO thin films and doped ZnO thin films deposition methods such as Sol-gel spin coating, sputtering, chemical vapour deposition, spray pyrolysis, and pulse laser deposition [4, 5, 6, 7, 8] but the well-known sol-gel spin coating process is relatively easy, cheap and not energy intensive.

In this work, results of the properties of annealed ZnO and F:ZnO deposited by the spin coating process are presented. The observed changes in the structural and optical characterization are shown as the functions of temperatures.

2. EXPERIMENTAL DETAILS

2.1 PREPARATION OF SOLUTION

All reagents used were analytically grade. ZnO was synthesized from Zinc acetate dehydrate [Zn $(CH_3COO)_2.2H_2O$] and fluorine was synthesized from ammonium fluoride (NH_4F). 121.5 g of Zinc acetate dehydrate was weighed and dissolved in 250 ml of methanol which serves as solvents. The solution was refluxed with a magnetic stirrer at 60ºC for 2 hours to yield homogeneous solution in a balloon flask which was tightly sealed.

121.5 g of zinc acetate dehydrate was weighed into a beaker afterwards 2 g of ammonium fluoride was added in which the ammonium fluoride serves as the dopants. The reaction was carried out with the use of methanol as solvent and monoethanolamine (C_2H_7NO, MEA) as a stabilizer. The solution was refluxed with a magnetic stirrer at 80ºC for 3 hours to yield homogeneous solution in a balloon flask which was tightly sealed. The two different solutions (ZnO and F:ZnO) were prepared and deposited on glass substrates. The same concentration of solutions was prepared for ZnO and F:ZnO but were annealed at different temperatures from 100ºC to 400ºC after been deposited on a glass slides by a spin coater. The combination procedure that resulted into different solution is shown below

Table 1: Solution preparation and chemical combination

Sample	ZnO & F:ZnO Concentration (M)	Solvent Ml (Methanol & mono-ethanol amine)	Solution Gramms(g)
ZnO	1.5	250 Ml	121.5 g
ZnO	1.5	250 Ml	121.5 g of ZnO and 2 g of NH_4F

2.2 Substrate Cleaning

The glass slides were clean with cotton wool, cleaning soap and distilled water, the slides were checked under the microscope to check if there were still more dirt and later clean with distilled water to remove the remaining dirt. The glass slides were soaked in ethanol for 30 minutes; this was done to remove all organic particles and solutions droplets. Finally the glass slides were put in an ultrasonicator at 69ºC for 5 minutes.

2.3 Spin coating

The spin coater used was a model Ws – 400BZ – 6NPP/AS and the process was carried out under a stream of compressed air. An amount of 1ml of dispersed solution was drawn into a syringe and dropped gently on the surface of the glass substrate repeatedly for five times, the solution was deposited on the whole surface of the glass substrate so as to have the thin film covering the total surface. The solution was dropped slowly and evenly on the surface of the glass substrate before the start of spinning.

The spin coater was set to rotate first at low speed to spread the liquid then at high speed, the spin coater was set at a speed of 4000 rpm for 30 seconds. The deposited glass substrates was sintered at 250^{o}C for 5 minutes to evaporate solvent and cooled to room temperature for both ZnO and FZnO.

This procedure was repeated 5 times to obtain the intended film thickness and quality and were cooled to room temperature and finally were annealed at 100 ^oC to 400 ^oC for 30 minutes.

2.4 Characterization

The optical properties of the thin films were carried out by using UV spectrophotometer (Model-AvaSpec-204B) in the wavelength 300 to 1000nm. Micro-structural analysis of the films was carried out by obtaining the SEM micrographs from the scanning electron microscope (Model ASPEX 3020).

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrographs of the film annealed at 100^{o}C, 200^{o}C, 300^{o}C and 400^{o}C respectively. For undoped ZnO thin films at annealed temperatures of 100^{o}C and 200^{o}C the films were well and evenly distributed across the substrate with more pores while thin films at temperatures of 300^{o}C and 400^{o}C were also evenly distributed with fewer pores. There was an indication that temperature increases the crystallinity of the films.This was due to the fact that increase in temperature increases the crystalinity of the thin film.

Figure 2 shows the micrographs of fluorine doped ZnO thin films for 100^{o}C and 200^{o}C, the films were well dispersed and less porous while 300^{o}C and 400^{o}C were dispersed and uniform across the substrate with distinct grains. Further examination of the micrographs showed that the grain size and densification of the particles increases with increase in temperature but the grain size for doped ZnO films was found to be more pronounced. The increase in the grain size of doped ZnO shows low lattice mismatch of Zn^{2+} and F^- as the ionic radius of F^- is 0.77 Å while that of Zn^{2+} is 0.74 Å. This shows that fluorine is an adequate anion doping candidate due to lower lattice distortion compared to Al, Ga or In [9].

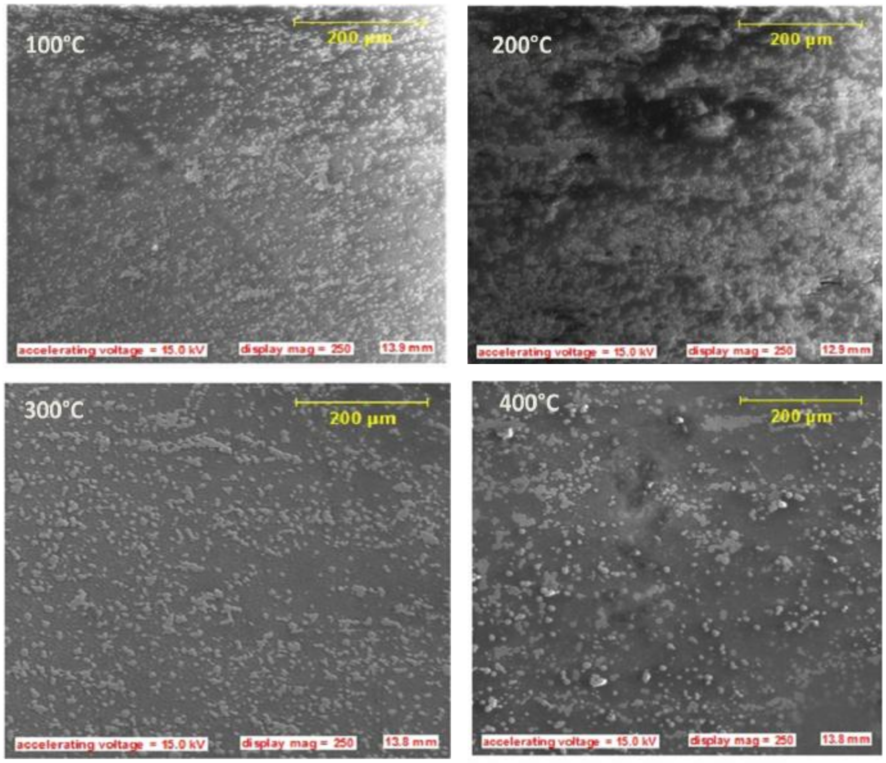

Fig. 1: SEM micrographs of undoped ZnO thin films for 100ºC to 400ºC temperature

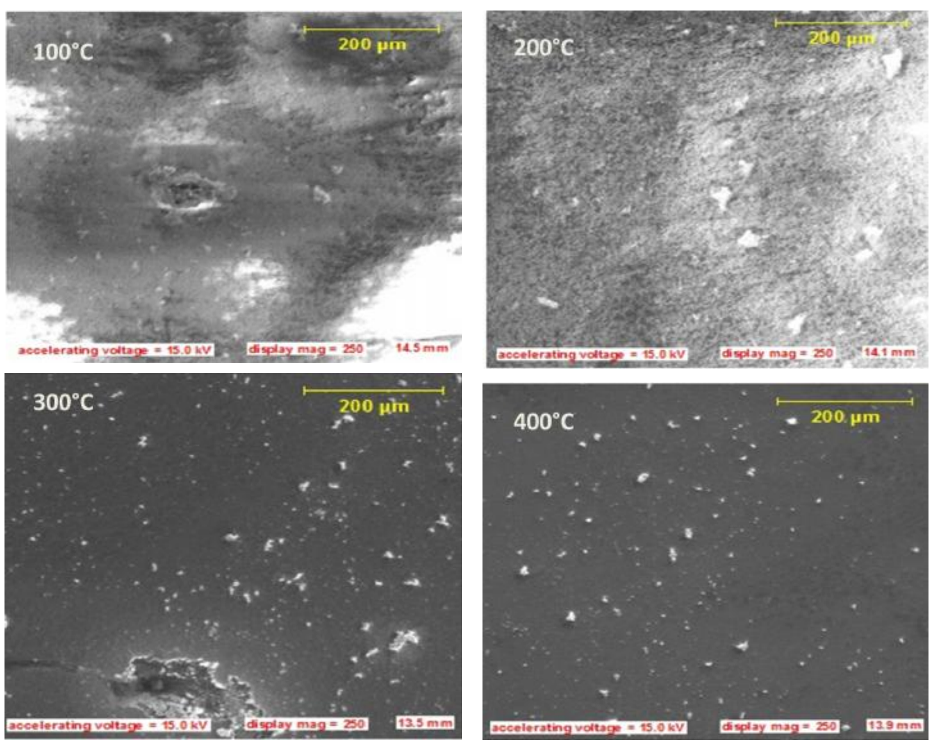

Fig. 2: SEM micrographs of flourine doped ZnO thin films for 100 ºC to 400 ºC temperature

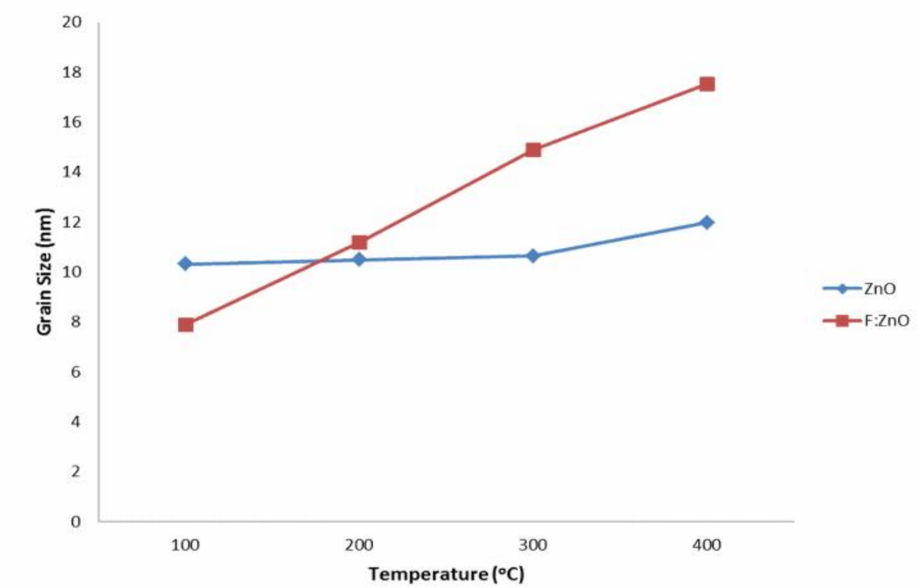

Fig. 3: Grain size for undoped and flourine doped ZnO thin films

The variations of grain size of both undoped and doped ZnO films were shown in figure 3. It was observed that as the temperature increases the grain size of the films also increases. In figure 4, the result of 400 ºC ZnO shows a higher transmittance of 85 % in the visible region which decreases with decrease in temperature to about 50 % for 100 ºC deposition. This is implies that generally there is increase of transmittance with increase in annealing temperature.

The optical transmittance T was calculated from the following relation

$$A = \log_{10} \frac{I_t}{I_o} = \log_{10} T \qquad (1)$$

where A (absorbance) is the logarithm to base 10 of the transmittance

Figure 5 shows a higher transmittance of 75% in the visible region and decreases gradually to about 55% for 100^{o}C. The decrease in transmittance may occur due to the increase of the particle size because of the progression of F in the ZnO thin films except for 200 ºC deposition which gave lower transmittance to 100ºC. The observed trend for 200^{o}C spectrum is as result of lower precursor. Comparing the undoped and flourine doped thin films, all films were highly transparent in the visible region of the electromagnetic spectrum and this increases with increase in temperature. The doped films have a reduced transmittance in the visible region compared with the undoped films which was due to the dopant. This is consistent with the fact that flourine concentration leads to intensity reduction in the visible region [9]. This suggest that the films have good optical quality due to low scattering or absorption losses making it suitable for opto-electronic applications.

Figure 6 shows the reflectance spectra of ZnO thin films. Low reflectivity of about 20% was shown in the UV region for 400 ºC deposition which reduces to about 7 % for 100 ºC deposition while in the visible region a higher reflectivity of 32 % for 400 ºC deposition reduces to 12 % for 100 ºC deposition. This generally low reflectivity is correlated to the fact that the films have highly absorbing property.

The relectance spectra of F:ZnO thin films are presented in Figure 7. It was observed that the reflectivity of F:ZnO for 100 ºC– 400 ºC deposition were very low in both UV and Visible region and this decreases rapidly with decrease in temperature and increasing wavelengths.

The optical band gap of all the films were calculated using the transmittance data obtained in the region between 300 nm to 1100 nm.

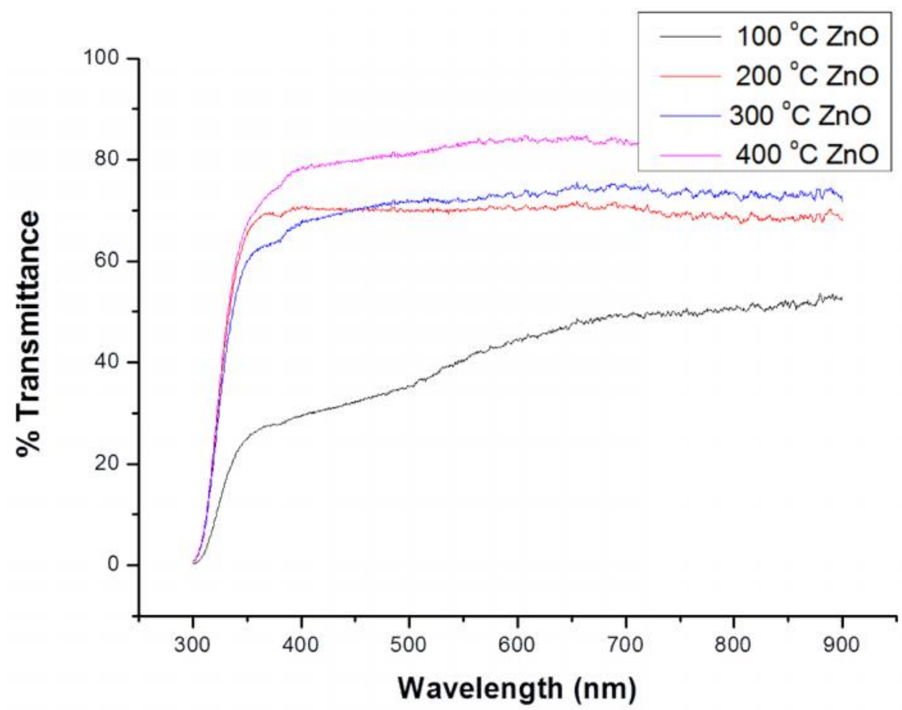

Figure 4: Transmittance Spectra of 100 ºC – 400 ºC undoped ZnO thin films

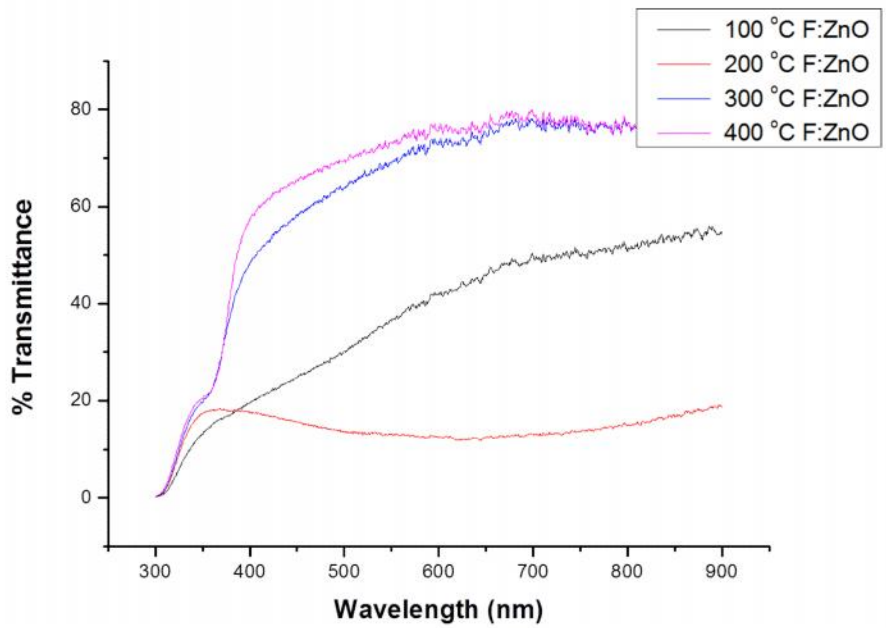

Fig. 5: Transmittance Spectra of 100 ºC – 400 ºC flourine doped ZnO thin films

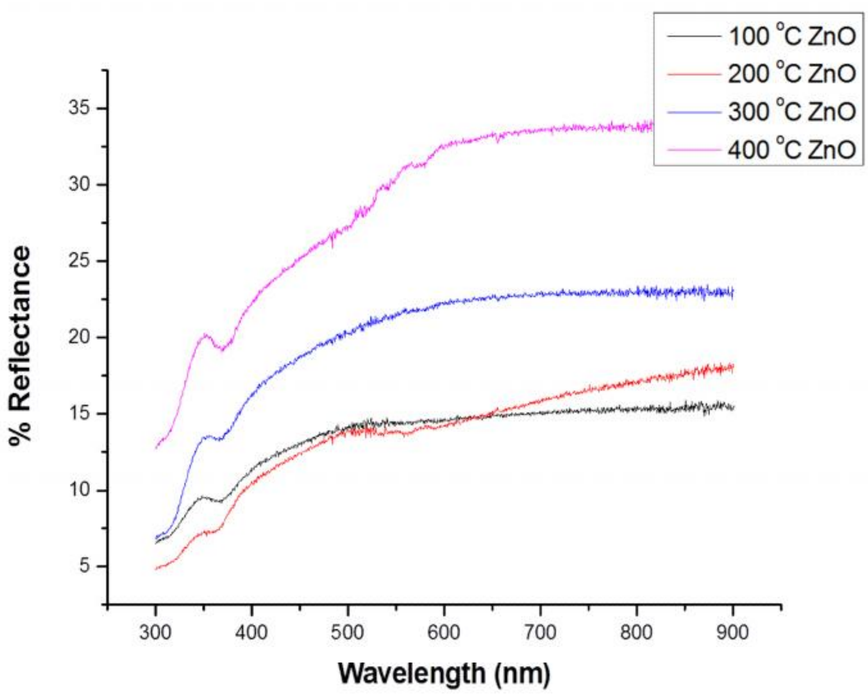

Fig. 6: Reflectance spectra of 100 ºC – 400 ºC undoped ZnO thin film

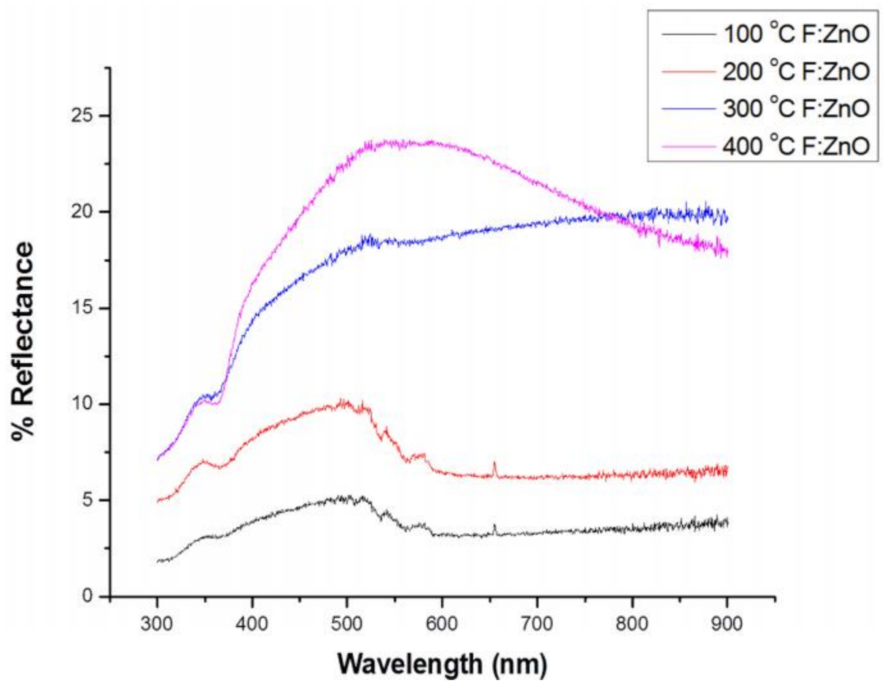

Fig. 7: Reflectance spectra of 100 ºC – 400 ºC Flourine doped ZnO thin films

From Figure 8, it was observed that a blue shift occurs as the temperature increases from 100 ºC to 400 ºC, E_g was found to be 3.80 eV, 3.90 eV, 3.95 eV and 4.0 eV respectively. 100 ºC to 400 ºC F:ZnO thin films as shown in Figure 9, reveals the increase in band gap energy by increasing the temperature. Eg was found to be 3.76 eV, 3.80 eV, 3.82 eV and 3.90 eV respectively. This observed trend suggests increase in improved crystal formation due to increase in temperature.

However, comparing undoped ZnO thin films and fluorine doped ZnO thin films, a red shift was observed. The red shift result shows the fact that flourine atoms are replacing the Zn atoms or competiting with Zn atoms sites. This observed trend also suggest increase in carrier generation, which is increased with the addition of flourine atoms. Hence, the band gap of ZnO can be tailored with the addition of flourine and varying temperature for engineering applications. Similar trend have been reported by [10] for Al:ZnO thin films.

The refractive index spectra for undoped ZnO thin films at temperature range of 100^{o}C- 400^{o}C is shown in Figure 10. The results shows an increase in the refractive index from 100ºC deposition to 400ºC deposition temperature in both UV and visible regions. The values of the refractive index are 2.2, 2.4, 2.8 and 3.75 respectively. The refractive index spectral for flourine doped ZnO thin films at temperature range of 100 ºC to 400 ºC is shown in Figure 11.

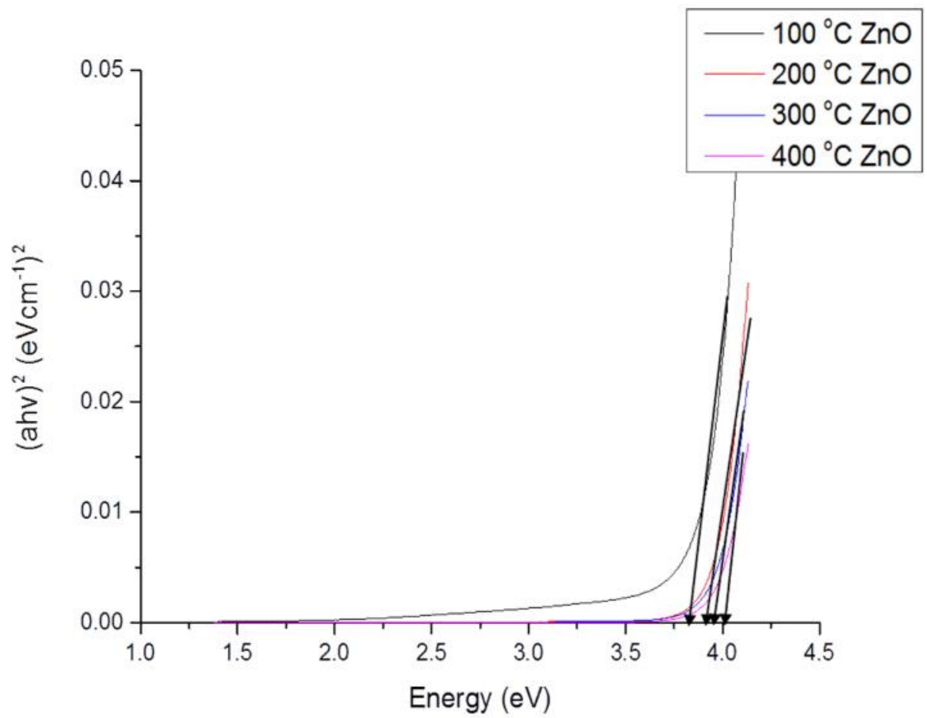

Figure 8: Optical band gap spectra for 100 ºC to 400 ºC undoped ZnO thin films

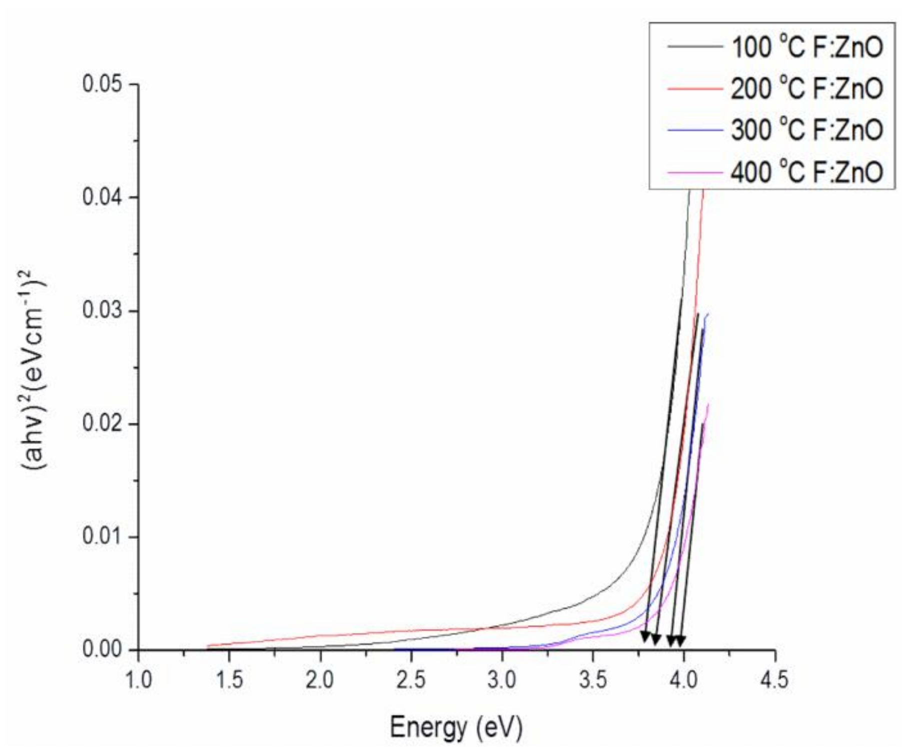

Figure 9: Optical band gap spectra for 100 ºC to 400 ºC flourine doped ZnO thin films

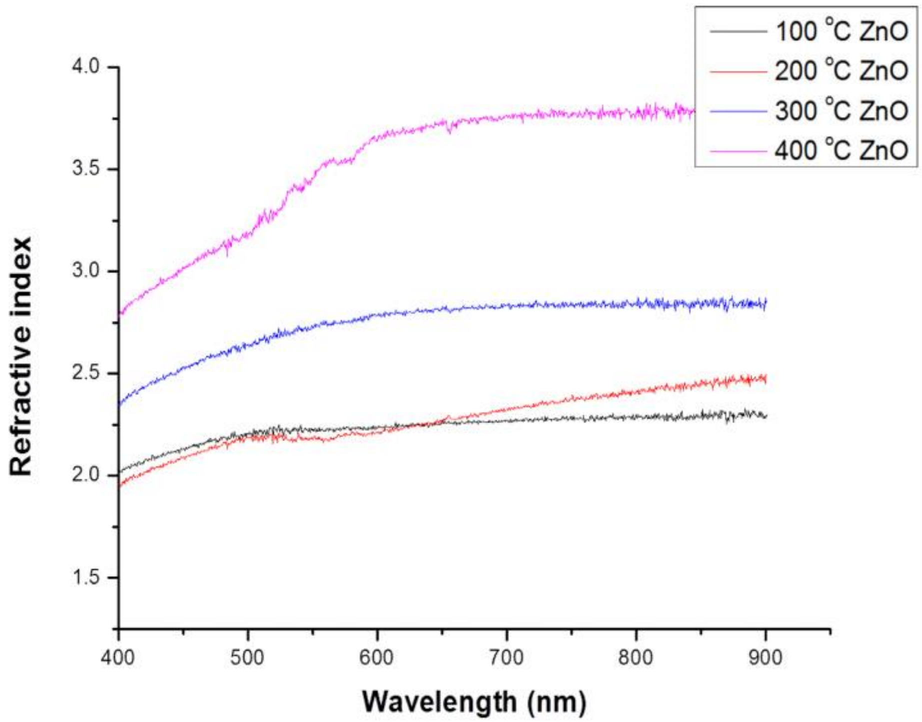

Figure 10: Refractive index spectra for 100 ºC to 400 ºC undoped ZnO thin films

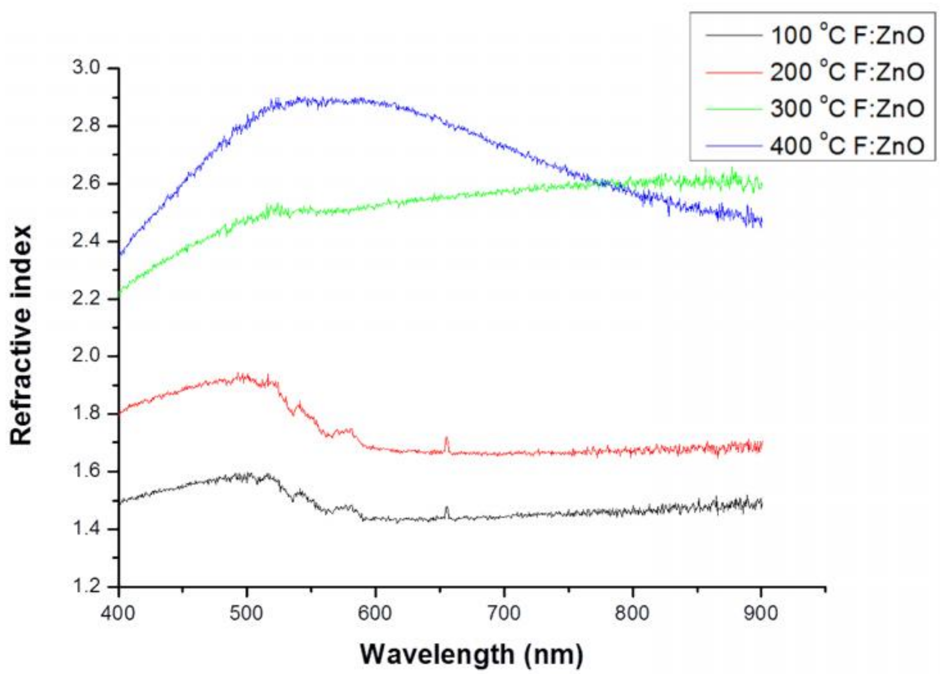

Figure 11: Refractive index spectra for 100 ºC to 400 ºC flourine doped ZnO thin films

The results shows an increase in the refractive index in both UV and visible regions. The values of the refractive index are 1.6, 1.9, 2.6 and 2.9 respectively. Comparing undoped and flourine doped ZnO thin films, there is a decrease in the refractive index of the ZnO thin films when doped with flourine.Therefore, we can say that, the value of the refractive index was found to be dependent upon the doping element and temperature.

Optical conductivity in semiconductors depends strongly on the optical bang gap. For thin films, the optical conductivity is dependent upon many parameters such as, the absorption coefficient, refractive index, the frequency of incident photons and the extinction coefficient.

100ºC to 400ºC undoped ZnO thin films optical conductivity spectra is shown in Figure 12. The results shows an increase in the optical conductivity in the UV region at wavelength λ < 400 nm which gradually decreases in the visible region from 100ºC deposition to 400ºC deposition temperature. From 100ºC to 400ºC flourine doped ZnO thin films optical conductivity spectra is shown in Figure 13. The results shows an increase in the optical conductivity in the UV region at wavelength λ < 400 nm which gradually decreases in the visible region from 100ºC deposition to 400ºC deposition temperature. Comparing undoped and flourine doped ZnO thin films, there is a decrease in the optical conductivity of the ZnO thin films when doped with flourine.This may be due to the dopant.

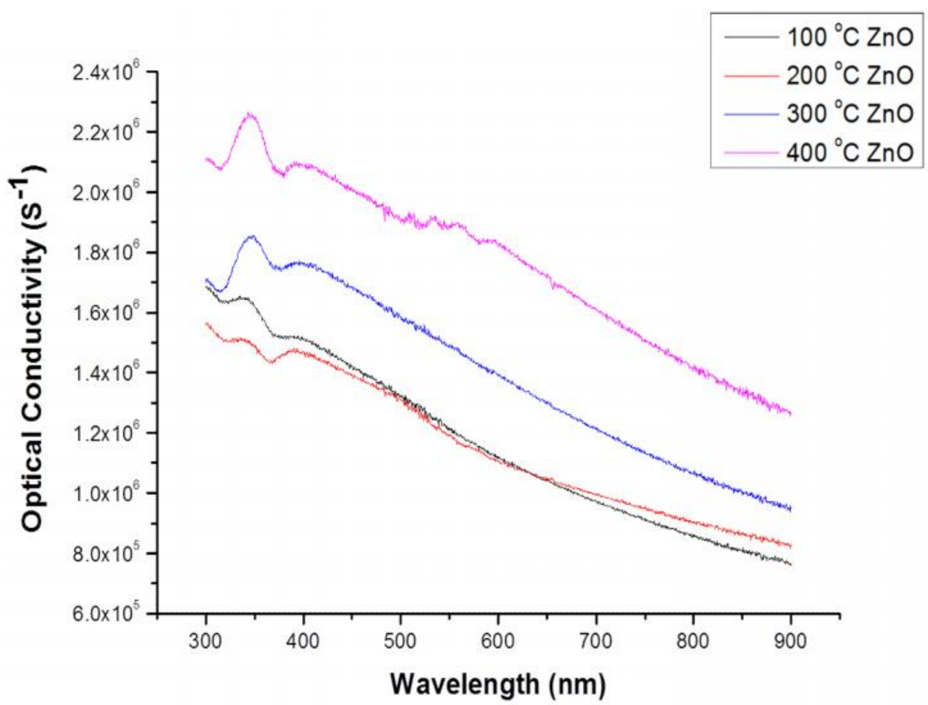

Figure 12: Optical conductivity spectra for 100 ºC to 400 ºC undoped ZnO thin films

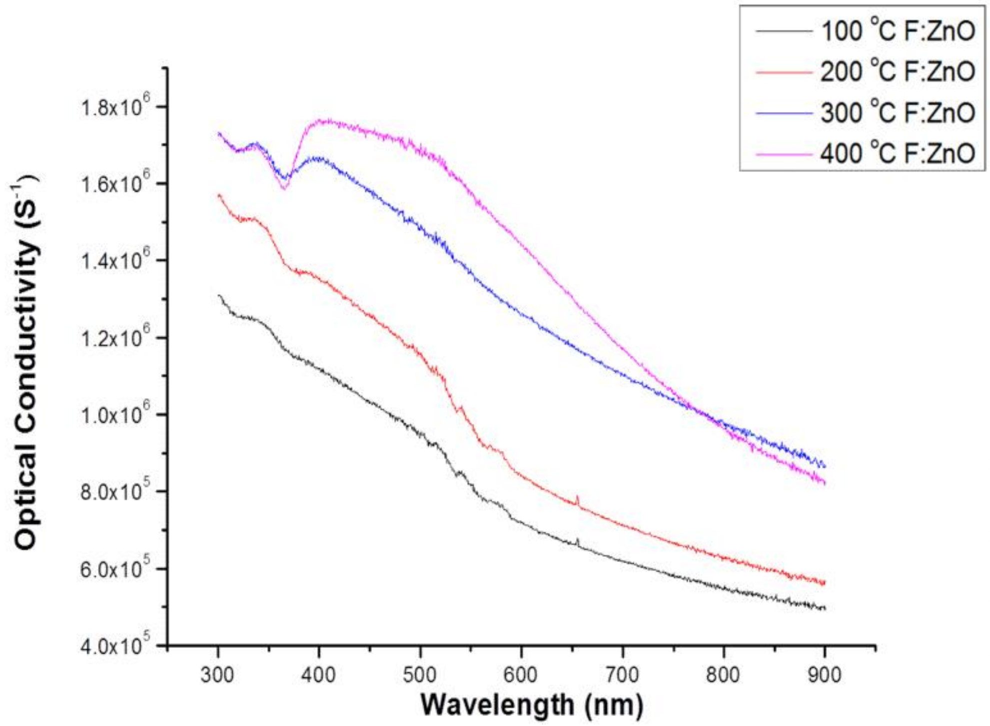

Fig. 13: Optical conductivity spectra for 100ºC to 400ºC fluorine doped ZnO thin films

4. CONCLUSION

ZnO and F:ZnO thin films have been successfully deposited using spin coating technique. Films were prepared by using the same concentration for both ZnO and F:ZnO but annealed the thin films from 100^{o}C to 400^{o}C. The prepared films showed wide energy band gap, transmittance spectra with films that are highly transparent while the reflectance spectra analysis showed that the films are low. The high value of transmittance showed that the thin films have good optical quality due to low scattering or absorption losses making it suitable for opto-electronic applications. The low reflectance at low temperature makes the thin film a good material for anti-reflective coatings and the wide band gap showed the films are good material for optoelectronic application.

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