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Impact of Post- Deposition Heat Treatment on the Morphology and Optical Properties of Zinc Oxide (ZnO) Thin Film Prepared by Spin-Coating Technique

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Abstract: This research work examines the structural and optical properties of ZnO thin films. Deposition were done by spin coating of solution of Zinc oxide onto pre-cleaned glass substrate at 4000 rpm for 30 sec using spin-coater under ambient condition at room temperature in order to form desired thickness of the film on the substrate. Post- deposition thermal annealing at different range of temperatures from 150°C to 600°C with steps of 50°C was carried out on the samples. The impact of thermal annealing on optical properties of the deposited thin film was investigated using UV-VIS spectrophotometer and scanning Electron Microscope for the morphology. The optical transmittance, reflectance, absorbance were recorded which was used to evaluate the optical band gap of Zinc oxide. Observation shows that band gap energy reduces as annealing temperature is increased from 150°C to 600°C. Observation made on the morphology using SEM model ASPEX 3020 showed that as the temperature increases the surface of the sample roughness increases. It was deduced that as the annealing temperature is increased the surface roughness increases. This may be due to increase in grain size with increase in annealing temperature. The band gap energy decreases as the annealing temperature increases.

Keywords: Spin-Coating, Thermal Annealing, Zinc Oxide, Morphology, Optical Properties

1. Introduction

Zinc oxide (ZnO) is an important semiconductor material that has its found application in organic electronics such as solar cells and optoelectronics to mention but a few [1]. The techniques that can be used to deposit ZnO on glass substrate includes Chemical Vapor Deposition (CVB), Spray pyrolysis, Thermal vacuum Deposition, Sputtering and the last but not the least Spin- coating [2]. Zinc oxide is an inexpensive n-type semiconductor which can be used as electron transporting layer in solar cells because it has high thermal and mechanical stability at room temperature coupled with chemical stability. It has broad range of radiation absorption and high photo stability. Zinc oxide (ZnO) is used as a heterogeneous catalyst, have a high catalytic activity, non-toxic, insoluble, and also a cheap catalyst [3 -4] which is an important n-type [5-7] semiconductor. ZnO is not only a material of particular interest because of its unique optical and electronic properties, but also it has some characteristics that include the following: (a) wide-band gap semiconductor [3-18], (b) large exaction binding energy of 60 MeV [5-7, 10, 12, 13, 19-20]. The interest in ZnO is as a result of its high abundance and the availability of potentially high quality low cost substrate layers of transparent ZnO films on which electronic processes solar cells and flat panel displays occur [21-30].

In this research work spin-coating method was employed to deposit the ZnO on the pre cleaned glass substrate, because it possesses several advantages, such a low temperature processing, easy coating of large area, and being suitable for preparation of porous films and homogenous multi component oxide films. The spin-coating conventional techniques involved the placing of pre- cleaned substrate on the stub of the spin- coater model laurel WS-650Hz-23NPP, set the program, dispense liquid, run the program under ambient condition at room temperature. Deposition was done by spin coating of solution of ZNO onto pre-cleaned glass substrate at 4000 rpm for 30 sec using spin-coater under ambient condition at room temperature in order to form 35nm thickness of the film on the substrate. The process of coating to drying was repeated to obtain the desired thickness of the film. Ethanol was used to dissolve ZnO powder because it evaporates in lesser rate than Methanol and also have no characteristic absorption and emission in the visible range. ZnO powder dissolved in Ethanol upon sonication for 3hrs for homogeneous mixture. The effect of thermal annealing on the morphological properties and optical properties of Zno thin films was studied using scanning electron microscope (SEM) model ASPEX 3020 and UV-VIS spectrophotometer Avantes model Avalight-DH-5-BAL.

2. Experimental Procedures

2.1. Materials

The materials used in this experiment were purchased from Sigma-Aldrich namely, ZnO powder and Glass slides.

2.2. Methods

2.2.1. ZnO Sample Solution Preparation

1ml Ethanol solvent was added into 81.38mg of ZnO powder from Sigma Aldrich. The solution then underwent ageing process for 3 hours upon sonication at room temperature without heat to allow homogeneous mixture and ZnO powder to fully dilute into solvent. Ethanol was chosen as a solvent because it has no characteristic absorption and emission in the visible range.

2.2.2. Substrate Preparation

Clean rectangular glass slides of dimension 25.4 mm by 76.2mm were used as substrates. The substrates were washed with detergent solution for 10 to 15 minutes and ultrasonically rinsed in water bath distilled water for 15 minutes at 30°C. The substrate was cleaned with Isopropanol acid [IPA] in ultrasonic bath for 15 minutes at 30°C and was blow-dried in Nitrogen environment.

2.2.3. Deposition of ZNO on the Substrate Using Spin-Coater

Place pre- cleaned substrate on the stub of the spin- coater Model WS-650MZ-23NPP, set the program, dispense liquid, run the program that is drop onto substrate, wait for several moments to enable solution to seep. Deposition was done by spin coating of solution of ZnO onto pre-cleaned glass substrate at 4000 rpm for 30 sec using spin-coater under ambient condition at room temperature in order to form 35nm thickness of the film on the substrate The process of coating to drying was repeated to obtain the desired thickness of the film.. The system rotates first at low speed to spread the liquid then at high speed to dry. This technique is cheaper and easier to use, it allows for uniform deposition unto flat substrate. Pre-heat deposited samples at 150°C for 1hr then slow cooling at room temperature to pyrolyze any unwanted ingredient other than ZnO.

2.3. Samples Characterization

The pre-heat deposited samples were annealed at different temperatures range from 150°C to 600°C for 60 minutes at step size of 50°C using Carbolite tubular furnance model Srw 21-501042 Type-CT17 and quenched at room temperature in Argon gas. One sample was untreated which is designated as control. Annealing is a heat treatment, involves heating a material to above its critical temperature, maintain a suitable temperature and then cooling. It can induce ductility, soften material, relieve internal stresses, refine structure by making it homogeneous and improve cold working properties. Optical transmittance and reflectance was measured using UV-VIS Avantes spectrophotometer model Avalight-DH-5-BAL for wavelength 200 and 1000nm. All samples were characterized to determine the optical spectrum for different annealing temperatures.

Mathematically A+R+T=1, A is the absorbance, R is the reflectance and T is the transmittance. To convert between the absorbance and transmittance, use the equation (1) below,

$$\text{Absorbance (A)} = 2\text{-}\log_{10\,(\%T)}. \quad (1)$$

The absorption coefficient of thin film is calculated from the formula (2) [31]

$$\alpha = 2.303\ (A/t) \quad (2)$$

Where, A is absorbance and t is the thickness [32]

The absorption coefficient α and the extinction coefficient k are related by the formula (3)

$$K = \alpha\lambda/4\pi \quad (3)$$

Where, λ is the wavelength. The variation of extinction coefficient k with wavelength is shown in figure 4. Zno is a direct –gap semiconductor. The optical band gap energy Eg and absorption coefficient α is related by the equation (4) [33]

$$(\alpha hv)^2 = hv — Eg \quad (4)$$

Where, α is the absorption coefficient and hv is the incident photon energy. Band Gap Energy (E) = hc/ λ where h = planks constant =6.626 x 10^{-34} joules sec. C= speed of light =3.0 x 10^{8} meter/sec. where1ev =1.6 x 10^{-19} joules (conversion factor).]. For calculation of the optical band gap of films, the curve of $(\alpha h\upsilon)^2$ vs. hυ was plotted. The energy band gap was obtained from straight line plot of $(\alpha h\upsilon)^{2/}$vs. hυ by extrapolating of the line to base line in figure 7 to figure 12

2.4. Optical Characterization

2.4.1. Transmittance

The optical transmittance of the samples was measured with an Avantes UV-VIS spectrophotometer. The spectrophotometer operates by providing a light source towards an aperture using an optical fiber and uses another aperture to measure the amount of light transmitted or reflected by the sample under test. Optical transmittance measurement was recorded with spectrophotometer in the wavelength between 200nm and 900nm. The transmittance spectrum is as shown in figure 1 to figure 3. The control is the untreated or un-annealed sample. The absorption spectra for ZnO thin films annealed at different temperatures is as shown in figure 4 It is deduced that as the annealing temperature increases there is increase in absorption of photon energy. It also shows that transmission increases as the wavelength increases and decreases with increases in annealing temperature. As the annealing temperature increases the absorption increases and as the wavelength increases the absorption decreases.

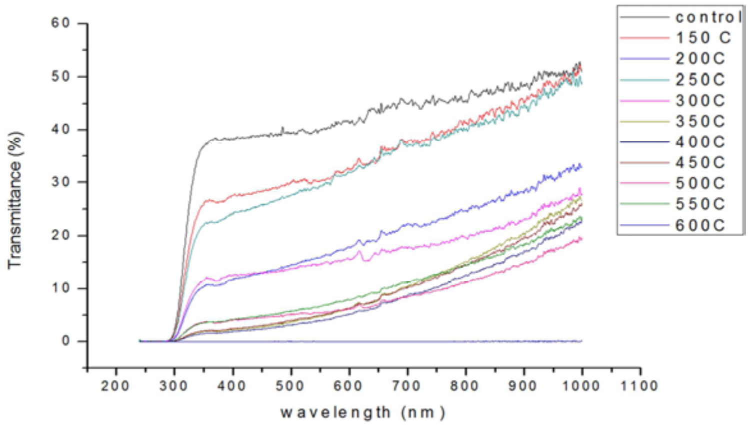

Figure 1. *Transmittance versus wavelength graph at different annealing temperature.*

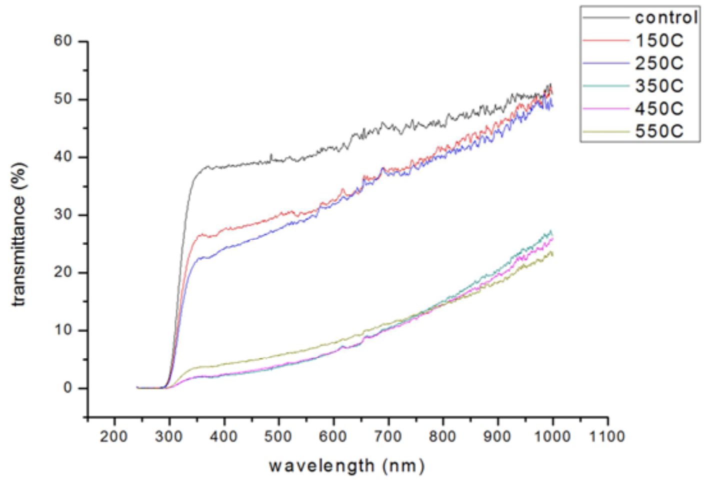

Figure 2. *Transmittance graph of selected temperatures.*

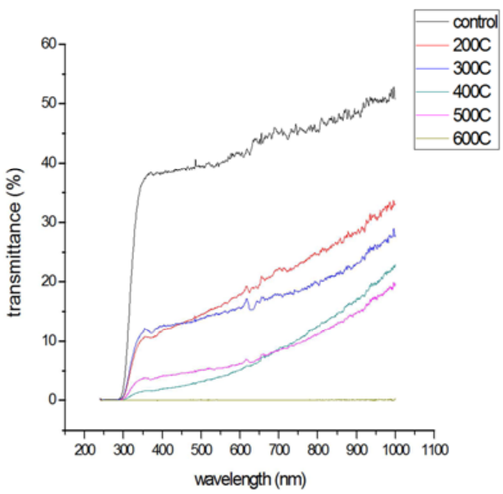

Figure 3. *Transmittance versus wavelength graph of selected temperatures.*

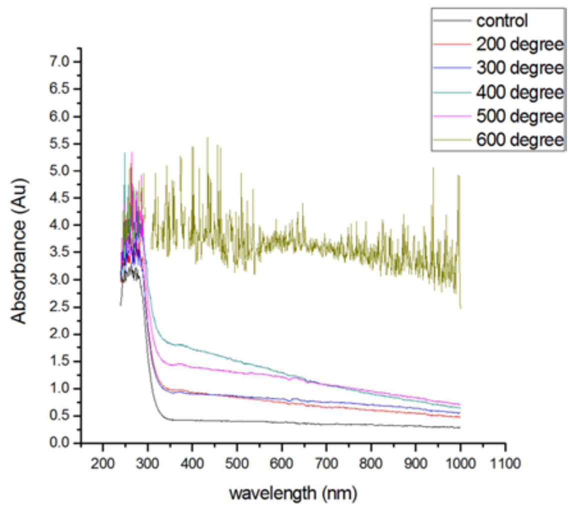

Figure 4. *Absorbance of ZnO thin films annealed at different temperatures.*

2.4.2. Absorption Coefficient

The absorption coefficient of ZnO thin film is calculated using this formula.

$$\alpha = 2.303\ (A/t)$$

Where A is the absorbance, t is the thickness. Extinction coefficient k is calculated

$$K = 2.303\ (A/t)\ \lambda/4\pi$$

The graph of extinction coefficient versus wavelength is shown in figure 5.

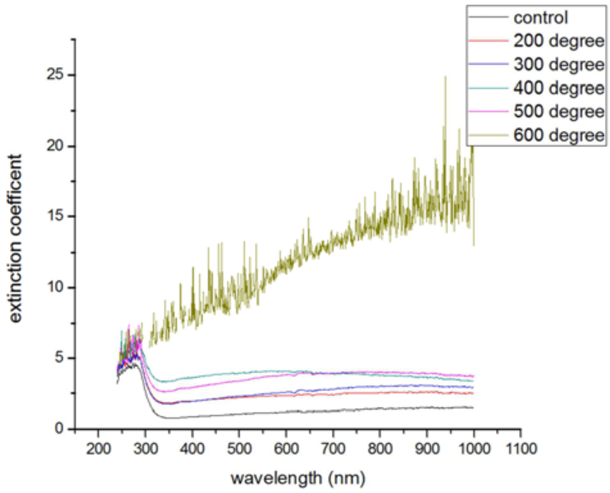

Figure 5. *Extinction coefficient graph versus wavelength for zno films annealed at different temperatures.*

2.4.3. Reflectance

The graph of ZnO thin films is as shown in figure 6.

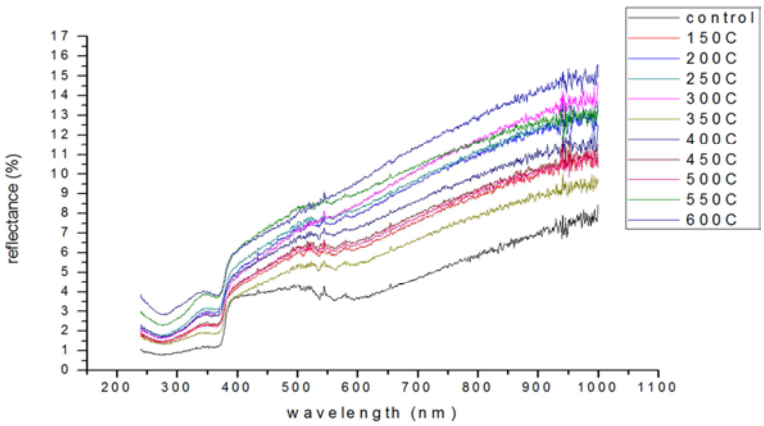

Figure 6. *Plot of reflectance versus wavelength graph.*

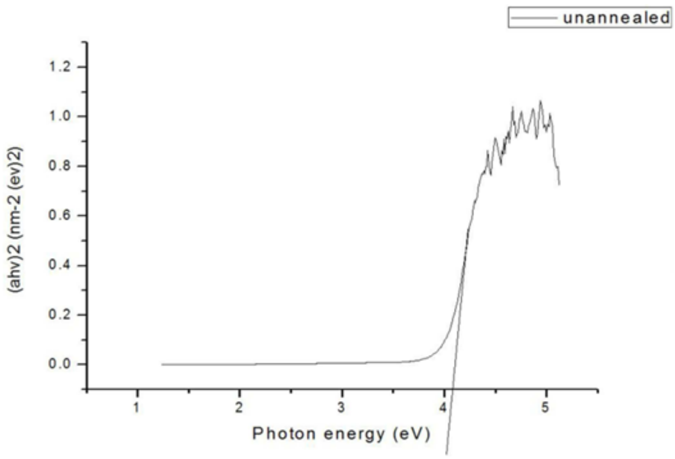

Figure 7. *Band gap energy graph of un-annealed ZnO thin film.*

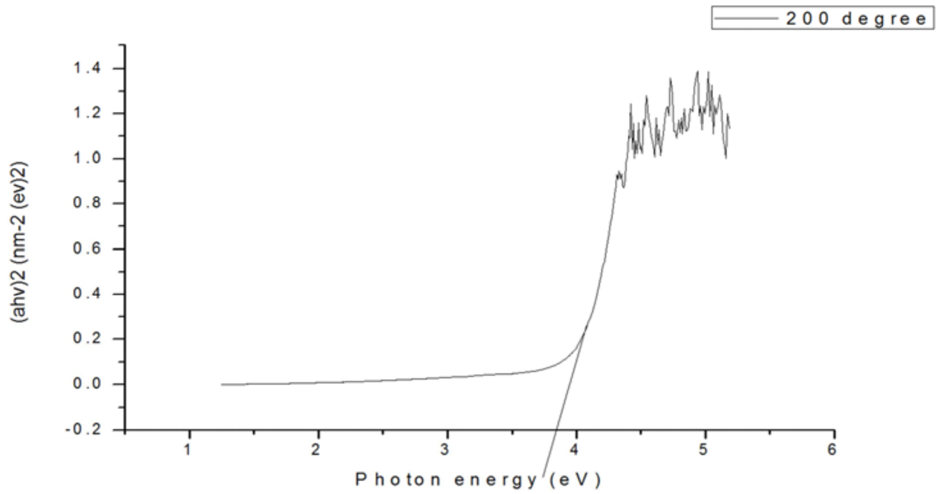

Figure 8. *Band gap energy of ZnO thin film annealed at 200°C.*

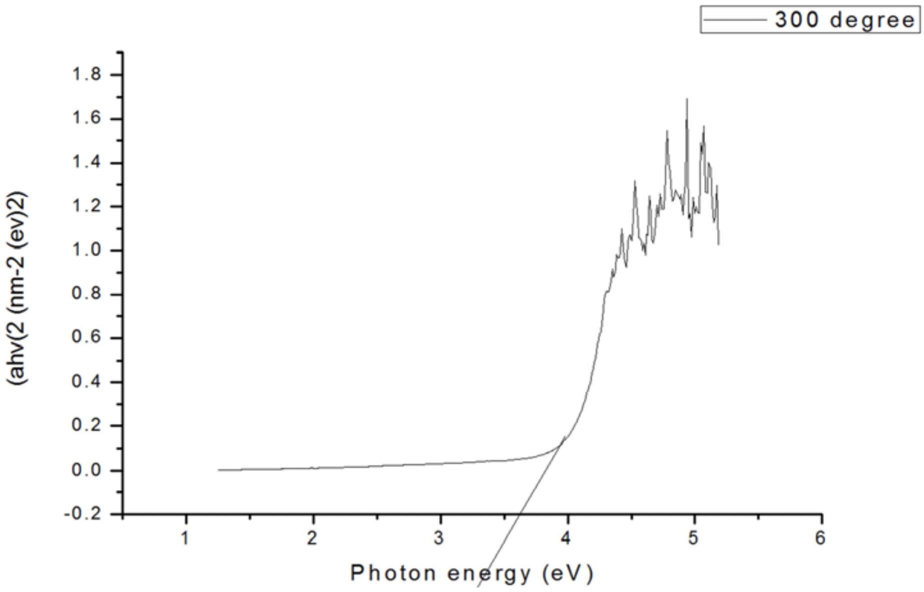

Figure 9. *Band gap energy of ZnO thin film annealed at 300°C.*

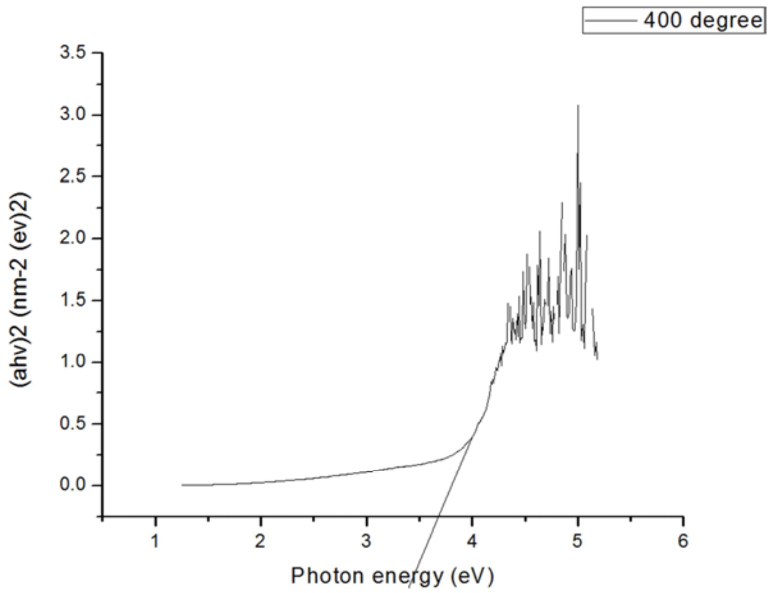

Figure 10. *Band gap energy of ZnO thin film annealed at 400°C.*

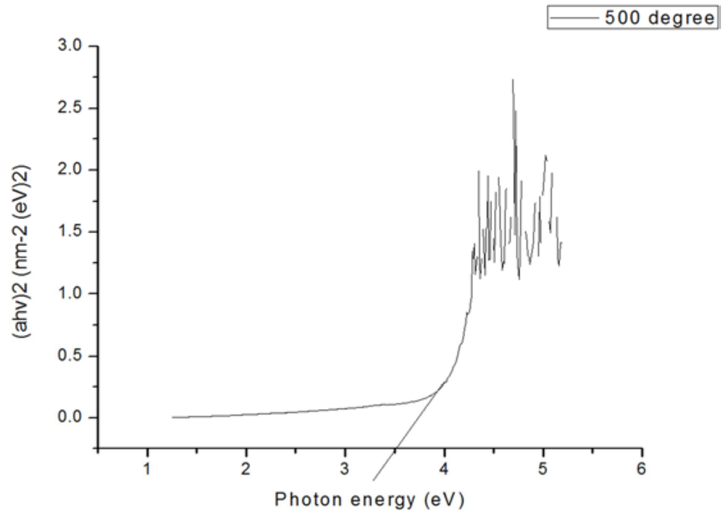

Figure 11. *Band gap energy of ZnO thin film annealed at 500°C.*

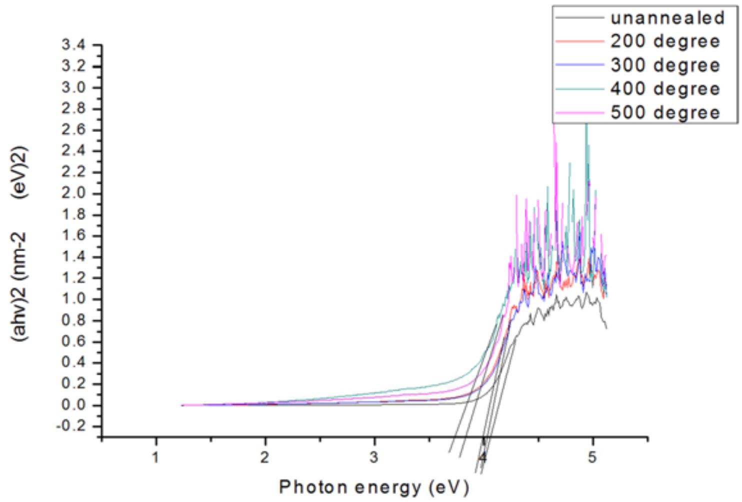

Figure 12. *Band gap energy of ZnO thin films annealed at different varying Temperatures.*

2.5. Morphological Characterization

Scanning Electron Microscope observation (SEM) model ASPEX 3020.

Scanning electron microscope (SEM) was employed to image the surface of the samples. All samples were appropriately cut to a size that can fit on the specimen stub of the SEM machine. SEM provides a useful means for investigating the morphological properties of the samples surface at desired magnification. To analyze the surface behavior of the sample. SEM morphology study of samples were carried out. Figure 13 to Figure 17 shows images of the sample at different temperature ranging from 150°C to 550°C in order to compare their surface morphologies with respect to the temperature variation. It was deduced that as the annealing temperature is increased the surface roughness increases. This may be due to increase in grain size with increase in annealing temperature. Figure 13 to figure 17 shows the morphological images at 150°C, 250°C, 350°C, 450°C, 550°C

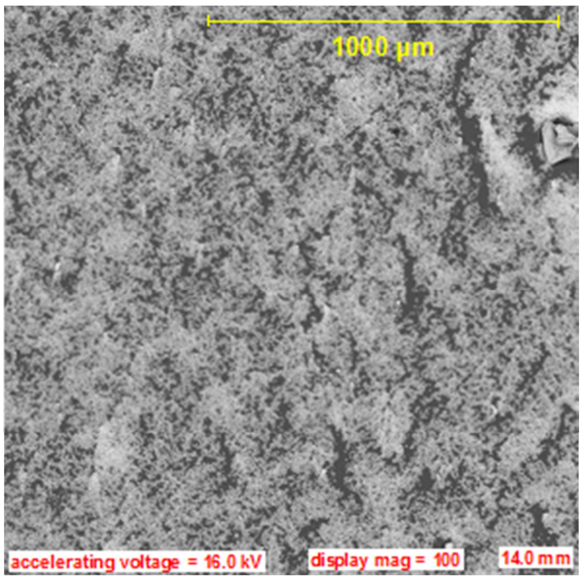

Figure 13. *SEM image of ZNO film annealed at150°C.*

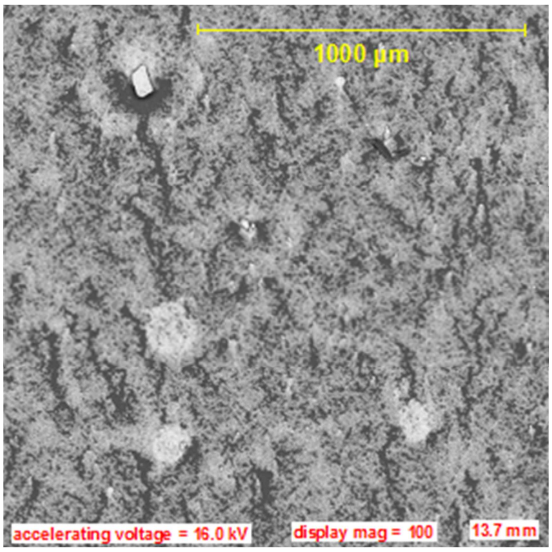

Figure 14. *SEM image of ZNO film annealed at 250°C.*

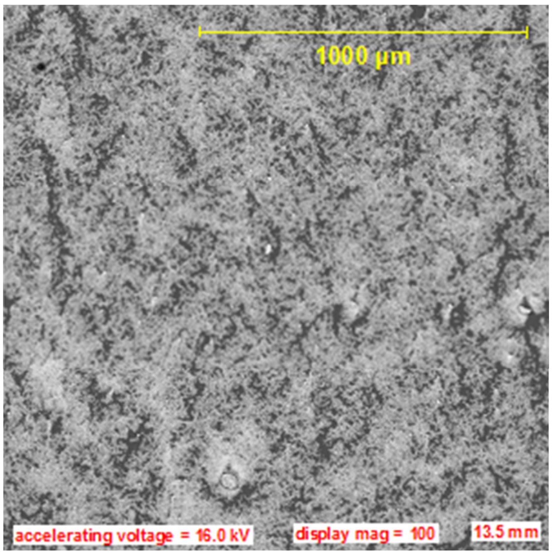

Figure 15. *SEM image of ZNO film annealed at 350°C.*

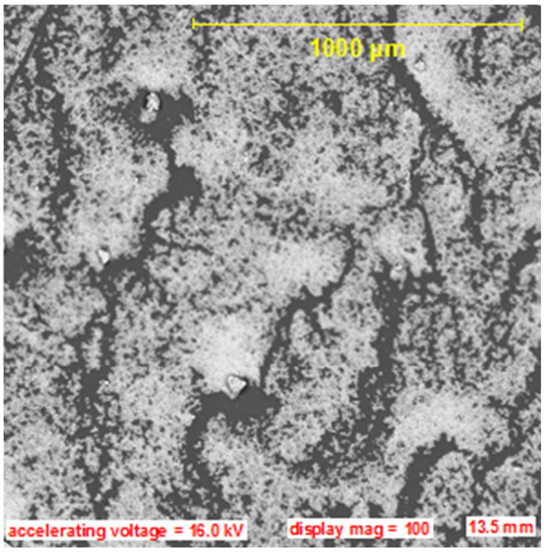

Figure 16. *SEM image of ZNO film annealed at 450°C.*

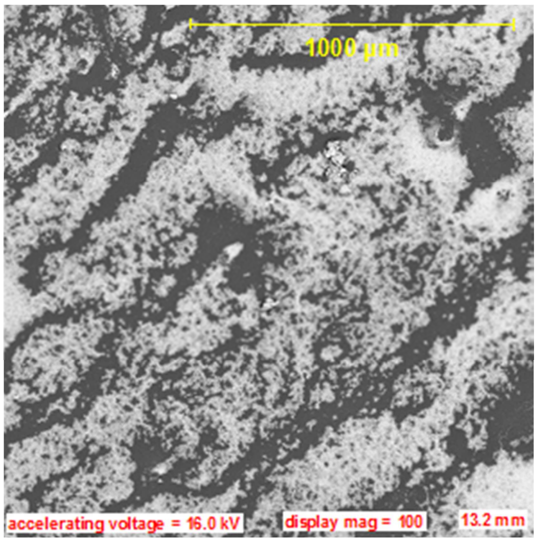

Figure 17. *SEM image of ZNO film annealed at 550°C.*

3. Result

It was deduced that as the annealing temperature increases there is increase in absorption of photon energy. It also shows that transmission increases as the wavelength increases and decreases with increases in annealing temperature. As the annealing temperature increases the absorption increases and as the wavelength increases the absorption decreases. Zinc Oxide thin films prepared on glass substrate by spin coating process and annealed at different temperatures from 150°C to 600°C step of 50°C. It was deduced that annealing temperature affects the morphological and optical properties of the ZnO thin films. The transmission spectrums of the films were recorded by UV-VIS Spectrophotometer. The films showed high transparency in the visible region. Extinction coefficients were calculated. The extinction coefficient showed some variation with rise in annealing temperature of ZnO films. The Optical energy band gap values were obtained by plot of $(\alpha h\nu)^2$ versus hν. The value of band gaps agrees approximately with that of bulk ZnO. As the annealing temperature increases the band gap value decreases. SEM image of the samples results the increase in roughness as annealing temperature increases, this is possibly because of increase in grain size, so that band gap energy Eg decreases.

4. Discussion

Transmittance of zinc oxide decreases with increase in heating temperature. There is optical stability of zinc oxide film in the visible absorption spectrum from 400nm to 700nm this will make zinc oxide suitable as buffer layer in solar cells. Photon absorption at 600°C has a waveform nature and decreases gradually compared to others annealed at lower temperature. Extinction coefficient of zinc thin film at 600°C rises steadily and linearly in a transient manner compared to a more stabilized nature of others annealed at lower temperature.

5. Conclusions

The morphology and the optical properties of zinc oxide were studied for unheated and heated thin films. The photon absorption upon heating zinc oxide was highest at 500°C in the visible spectrum. Extinction coefficient of zinc oxide at 500°C was the highest in the visible spectrum. The band gap energy decreases with increase in heating temperature from 4.03 eV to 3.5eV. An important observation was noted at 600°C, that heating zinc oxide on a glass substrate near or above the glass substrate melting point leads to transient fluctuation in absorption of photon energy of zinc oxide. The shortcomings called for alternative substrate at higher annealing temperature above 500°C. ASPEX 3020 Scanning Electron Microscope was used to study the morphology of the thin film and the results shows as the annealing temperature increases the roughness of the surface of zinc oxide thin film increases.

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