EVALUATION OF THE STRUCTURAL AND OPTICAL CHARACTERISTICS OF ZINC OXIDE POWDER PREPARED BY CO-PRECIPITATION METHOD

Amy Aung[1], May Kalayar Kyaing[2], Hnin Yu Wai[3], Moht Moht Than[3]

Abstract

In this research work, nano-sized Zinc Oxide powder (ZnO) were prepared by using Zinc Chloride and Sodium Hydroxide as the precursors and annealed at different temperatures at 400°C, 500°C and 600°C respectively. Structural and optical properties of the observable ZnO powders were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Ultraviolet visible spectrophotometer (UV-vis).By XRD analysis, Zinc Oxide revealed hexagonal wuritze structure nature. It was found that with increasing the annealing temperature the particle size increased about 38~41 nm by using Debye Scherrer's equation. Lattice strain, c/a ratio and dislocation density parameters were obtained from XRD analysis results. According to the average crystallite size, the size of the particles increases as the annealing temperature is increased. The SEM results have visualized the morphology of ZnO nanoparticles with irregular spherical in shape and highly agglomerated. To investigate the optical results of the grown Zinc oxide, the absorption spectra are evaluated in the ultraviolet-visible (UV-Vis) range. Based on the optical analysis results, the energy band gap of different annealing temperature samples was calculated from the linear extrapolated line of $(\alpha h\gamma)^2$ vs. $h\gamma$ plot.

Keywords: XRD, SEM, UV-vis, Debye Scherrer's equation and spherical in shape.

Introduction

Zinc oxide (ZnO) Nanopowders are multifunctional material which is known as n-type semiconductor with wide energy band gap is used as transparent conductive oxide (TCO) layer in organic and non-organic photovoltaic cell preparation. The families of II-VI nanoscale semiconductors of ZnO material which have a wide band gap and allow devices to operate at higher temperature. In photo electronic fabrication field, Zinc Oxide is recently useful in high research field.

Nanostructures Zinc Oxide is widely used in a number of applications like varistors, UV lasers, gas sensors, photoprinting, electrochemical nanodevices, sunscreen lotion cosmetics, medicated creams, solar energy conversion, optoelectronic devices, catalysis, gas sensors, etc. Zinc Oxide is key element for many industrial processes like paints, ceramics, rubber, soap, textiles and floor coverings.

There are various methods for the preparations of ZnO nanopowders like chemical co-precipitation method, sol-el method, thermal decomposition, hydrothermal method, chemical vapor deposition and electrochemical method. Among the different techniques, the co-precipitation approach to be one of the most promising methods to prepare ZnO nanoparticles due to its interesting properties like wide band gap of 3.39 eV.The as-prepared powders were

[1] Dr, Assistant Lecturer, Department of Physics, University of Yangon
[2] Assistant Lecturer, Department of Physics, University of Yangon
[3] Assistant Lecturer, Department of Physics, University of Yangon
[3]Associate Professor, Department of Physics, Mohnyin Degree College

annealed at different temperatures (400˚C, 500˚C and 600˚C) and obtained pure wurtzite hexagonal phase ZnO powder particles.

However, the co-precipitation method became a very attractive preparation method due to simple equipment involved and low cost compared to other techniques. The phase formation behaviour and the microstructures evolution of the samples are investigated by using X-ray diffraction (XRD) and Scanning Electron Microscope (SEM), respectively. The optical characteristics are analyzed by using UV-visible absorption spectrometer.

Experimental Procedure

The synthesized nanoparticles zinc oxide powders are characterized to investigate their microstructures and optical properties. The crystallinity and the phase composition of as-prepared were examined with X-Ray diffractometer, (MD-10) (Rigaku, Japan). The size of the particles and morphology of ZnO were studied by Scanning Electron Microscopy (JEOL-JSM 5610LV). Optical transmission and absorption spectra of ZnO were recorded using Shimadzu UV-Vis spectrophotometer (UV-1800).

Preparation of Zinc Oxide solution

In this process, the starting materials used were zinc chloride ($ZnCl_2$) and sodium hydroxide (NaOH). Aqueous solution was prepared by dissolving 6.8 grams of zinc chloride in 100 ml of distilled water. It was stirred continuously with magnetic stirrer for 30 minutes in ambient atmosphere so that zinc chloride can be dissolved properly. After 30 minutes stirring, the temperature was raised to 80˚C for 2 hours. Sodium hydroxide 5 grams was dissolved in 25 ml distilled water. The prepared aqueous solution of sodium hydroxide was added slowly drop by drop (dropped for 45 minutes) into the stirring solution zinc chloride solution by touching the walls of container/vessel under continuously stirring.

The reaction was allowed to proceed for 1 hour after complete addition of sodium hydroxide and then removed the magnetic stirrer from the container. After that the mixture solution was heated for 1 hour at 60 ~ 80˚C without stirring. A milky white solution was obtained which the reaction was allowed to proceed for 3 hours after complete addition of sodium hydroxide. The precipitate obtained was washed with distilled water many times and filtered using filter paper. The mixture was dried in air at 70˚C for 3 hours. The sample powders were annealed for 1 hour at different temperatures 400˚C, 500˚C and 600˚C respectively. The reaction equations are as follows;

$$ZnCl_2 + 2\ NaOH \rightarrow Zn(OH)_2 + NaCl$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

The flow diagram of sample preparation of ZnO powder was shown in Figure 1. Figure 2 shows the photograph of sample preparation sequence for ZnO powder using the simple co-precipitation method.

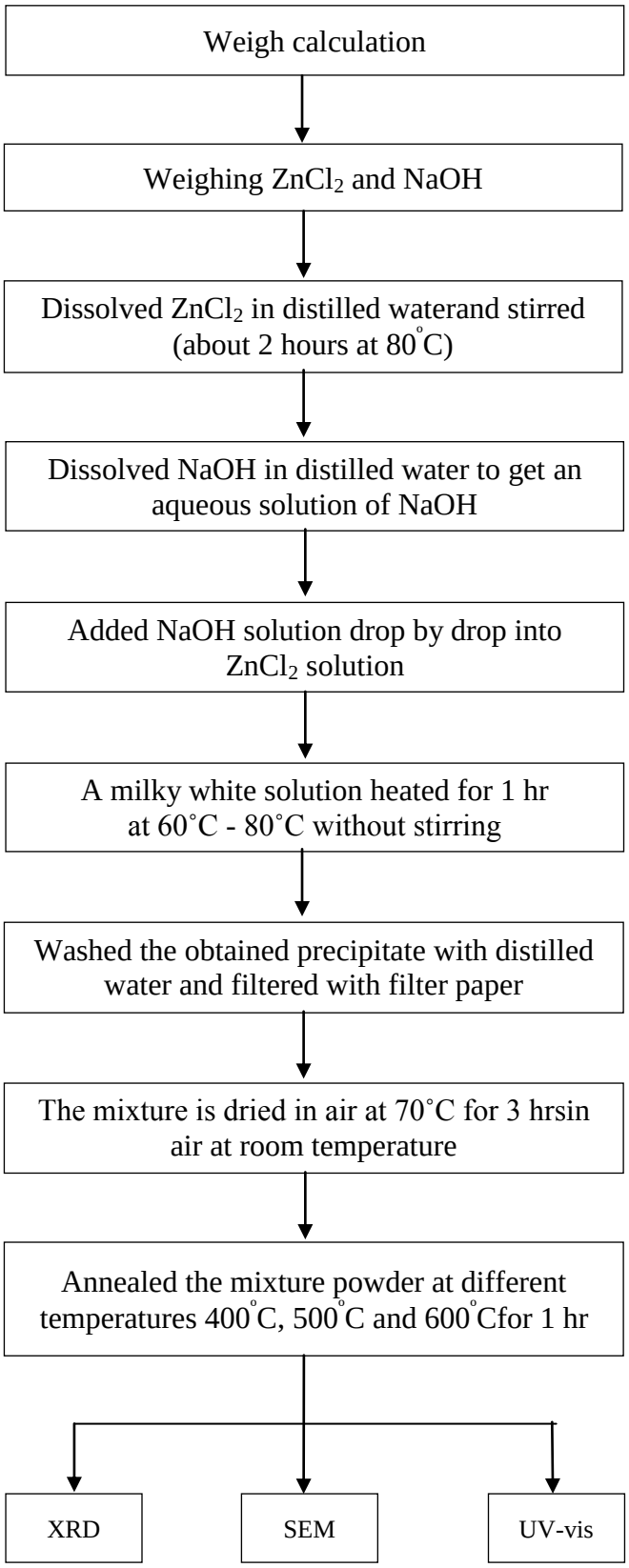


Figure 1 Flow diagram of sample powder preparation

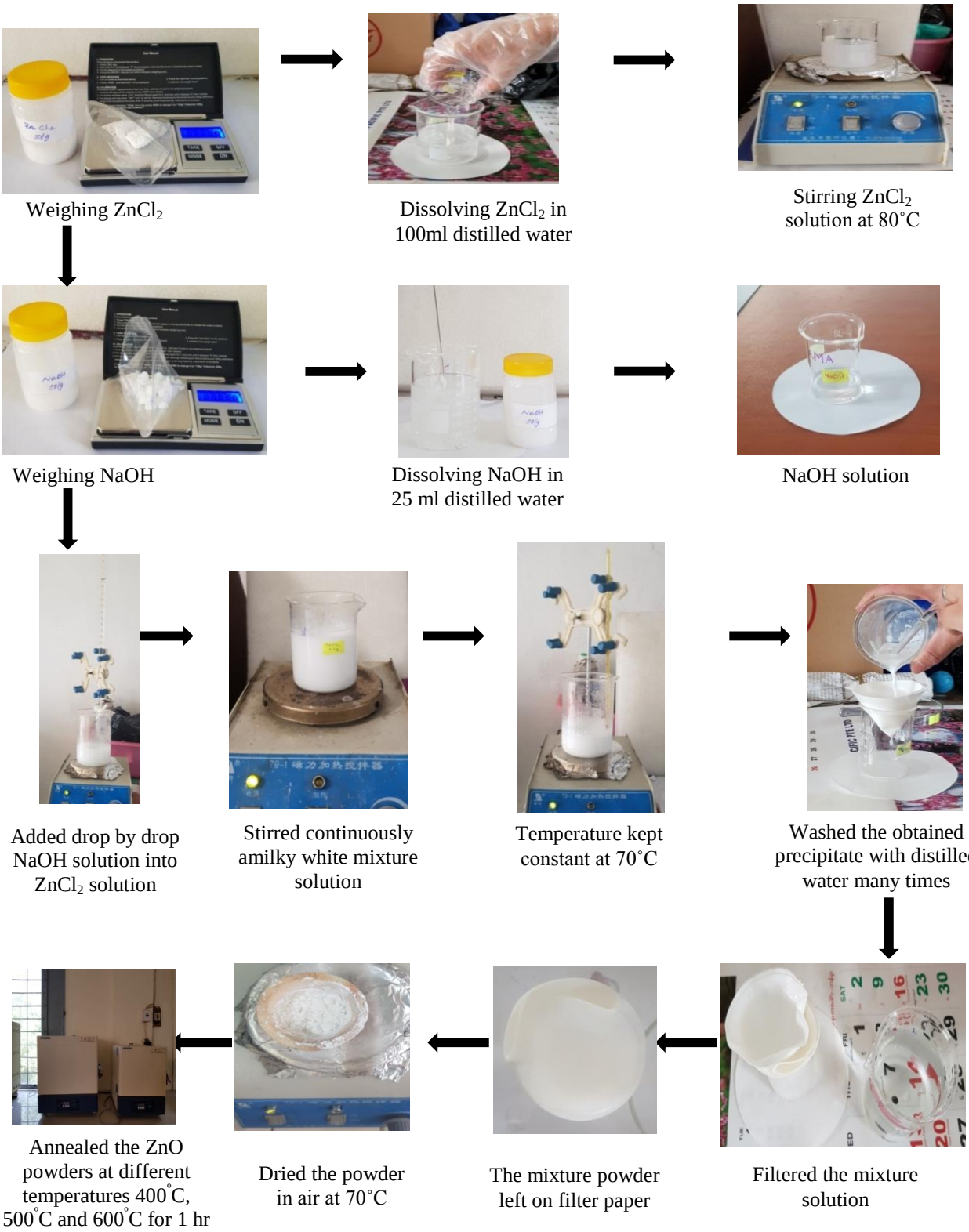


Figure 2 The photograph of sample preparation sequence for ZnO powders by using simple co-precipitation method

Result and Discussion

XRD Analysis

The XRD patterns of the obtained ZnO powders with different annealing temperatures at400°C, 500°C and 600°C labeled as sample 1, 2 and 3 were shown in Figure 3 (a), (b) and (c). All diffraction peaks can be indexed to the hexagonal wurtzite phase of ZnO crystals a match well with standard data.

The pattern suggests that the ZnO samples with different annealing temperatures are constituted in hexagonal wurtzite structure with a preferred orientation of (101) diffraction plane. No additional peaks correspond to the other impurities were detected in the XRD pattern, such as Zn and O are found in XRD patterns confirming that all the samples exist as main ZnO phase. The phase of ZnO powders can be prepared at different annealing temperaturesat400°C, 500°C and 600°C for 1 hour.

The detected peaks at scattering angles (2θ) values at 31.7˚, 34.4˚, 36.3˚, 47.5˚, 56.6˚, 62.8˚and 66.4˚ which corresponds to (100), (002), (101), (102), (110), (103) and (200) crystal plane respectively.

To identify the effect of annealing and investigate the reason for the diffraction peak shift the lattice parameters (a and c) were estimated from the relation. The experimental average lattice constant a and c of ZnO powders for lattice planes were determined as at400°C (3.2546, 5.2141), 500°C (3.2484, 5.2035) and 600°C (3.2491, 5.2041) respectively, giving average lattice constant as a =3.2507, c= 5.20723 Å. These values were very close to ZnO ones in the JCPDS card result, i.e, a = 3.264Å and c = 5.219Å.

The mean ratio c/a of ZnO powders were 1.602, 1.601 and 1.601. The values of the lattice parameter 'a' and 'c' decreased with an increase in annealing temperature, attributed the decrease in the values of lattice parameter to the lattice contraction that may have resulted from the presence of dangling bonds on the surface of ZnO. The above structural analysis reveals that an annealing temperature of 500°Cessentially required to obtain ZnO powders with high crystallinity quality and minimum stress.

The sharp diffraction peak of ZnO (101) plane was much stronger than the other peaks. The average crystallite size of the prepared nanopowder ZnO were calculated using the Debye-Scherer formula,

$$D = \frac{0.9\lambda}{\beta \mathrm{Cos}\theta}$$

Where D is the crystallite size, λ is 1.5406Å for $CuK_{\alpha 2}$, β is the full width at half maximum (FWHM) of the peak in radian and θ is the Bragg angle indicated the calculated particle size of the ZnO diffraction peak. The average crystallite size of the samples 1, 2 and 3 was found to be 38.15nm, 41.38nm and 41.17nm respectively. It was observed that the crystallite size of ZnO nanaopowders increased during annealing point out to the tendency of large grain growth in the nanoparticles that occurs as a result of movement of atoms to the favorable positions to merge into adjacent particles forming larger particles due to annealing.

ZnO powder annealed at 500°C registered the highest intensity, indicative of most enhanced crystallinity and grain growth. Increased in temperature to 600°C, the intensity fell slightly causes to grain boundaries resulting into a little poor crystallinity.

The decreased in the FWHM of the diffraction peaks with the increase of the annealing temperature can be attributed to the coalescences of grains at higher annealing temperatures. The shift to a higher angle of diffraction peak (101) with the increase in annealing temperature is occasioned by a change in stress in the ZnO and may be related to decrease of lattice parameters that come from the oxygen deficiency and strain caused by crystallinity during annealing process.

Additionally, ZnO nanopowders known to have defects such as zinc antisites, oxygen vacancies and lattice disorders, which are reported to disappear with annealing resulting to the contraction of lattice. It was observed that the diffraction peak (101) of the annealed samples were located at a higher diffraction angle, which meant smaller d value. During annealing, oxygen vacancies were generated while the majority of Zn atoms were in the same valence state. It was suggested that oxygen vacancies might reduce the lattice strain and corresponding lattice parameters, at least the c value.

The dislocation density (δ), which represents the number of defects in the sample is defined the length of dislocation lines per unit volume of the crystal and is calculated using the following equation;

$$\delta = \frac{1}{D^2}$$

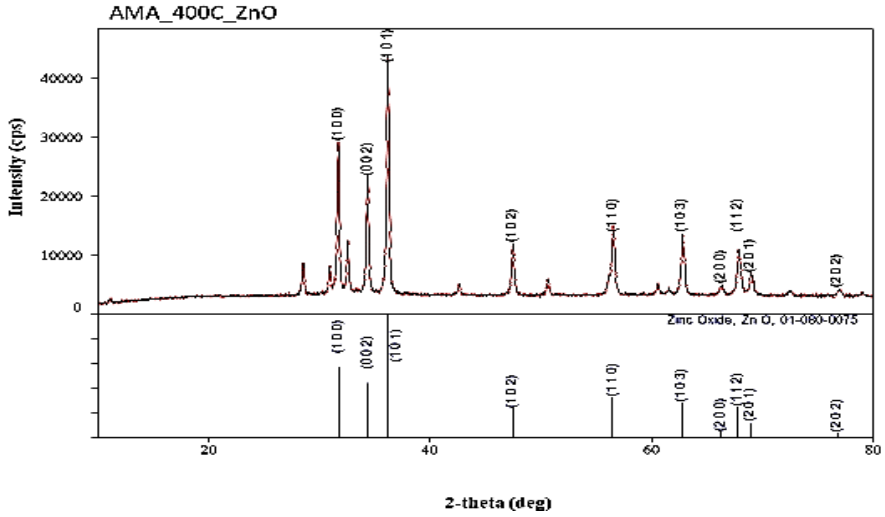
Where D is the crystallite size. The dislocation density for ZnO films annealed at different temperatures at 400°C, 500°C and 600°C were 6.87×10^{14} m^{-2}, 5.84×10^{14} m^{-2} and 9.82×10^{14} m^{-2}.In addition, the micro strain (ε) of samples were calculated by the following equation;

$$\varepsilon = \frac{\beta Cos\theta}{4}$$

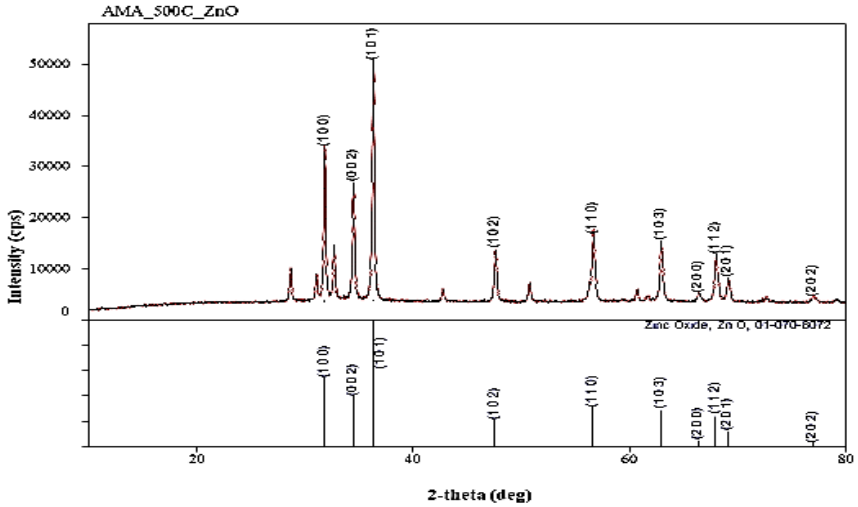
The macrostrains of the ZnO powders were 9.08×10^{-4}, 8.37×10^{-4} and 10.86×10^{-4} at 400°C, 500°C and 600°C.Table 1 summarized XRD analysis results of ZnO samples at (101) planes.

Table 1 The energy gap, grain size and crystallite size of ZnO powdersat (101) planes

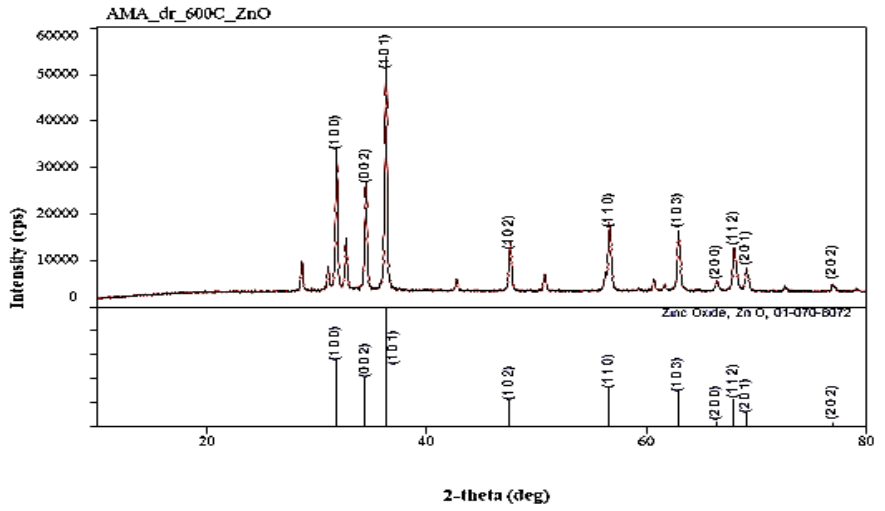
Sample	Annealing Temp:	(hkl)	FWHM	c/a ratio	Grain Size (μm)	Crystallite size (nm)	Energy Gap (eV)
1	400°C	(101)	0.219	1.602	0.32	38.15	3.15
2	500°C	(101)	0.202	1.601	0.47	41.38	3.39
3	600°C	(101)	0.203	1.601	0.40	41.17	3.84



(a) sample 1



(b) sample 2



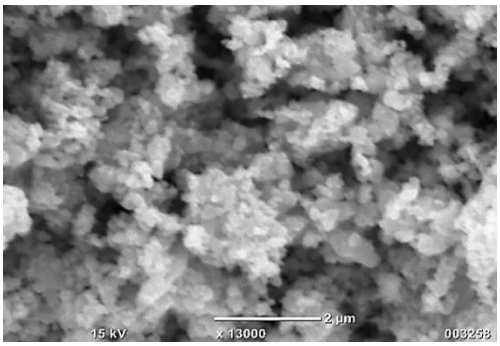
(c) sample 3

Figure 3 XRD patterns of ZnO powders annealed at 400°C, 500°C and 600°C for 1 hour (a) sample 1 (b) sample 2 and (c) sample 3

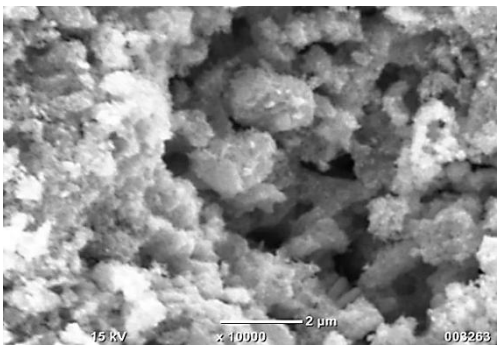
Scanning Electron Microscopy (SEM)

The investigation of microstructural properties such as grain size, pore and homogeneity are checked by SEM. Figure 4 shows the surface morphology at temperature ranging from 400°C to 600°C. The particle of ZnO powder with the range particle size of 0.32µm, 0.47µm and 0.40 µm for samples 1, 2 and 3. All ZnO powder samples tend to spherical shaped nanoparticles. As the temperature is increased further the shape of the particles is changed and size of the particles also increases. Reaction temperature is an important parameter which influences the structural morphology of the particles as well as the particle size.

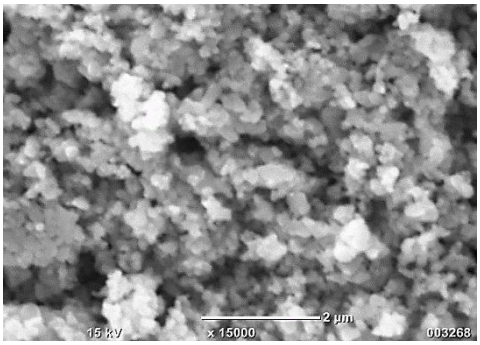
As the annealed temperature is increased there is increase in the particle size. In heating process when the particles are formed, they collide and either coalesce with one another to form a larger particle or coagulate. The grain size growths of ZnO powders observed mostly probably based on the shape and distribution of grain for each powder. The average grain sizes of the ZnO particles for the samples are shown in Table 1. As the temperature increased further the shape of the particles is changed and size of the particles also increases. The measurement of Scanning electron microscopy analysis by using the aid of "image J" software.



(a) sample 1



(b) sample 2



(c) sample 3

Figure 4 SEM images of ZnO powders at different annealing temperatures 400˚C, 500˚C and 600˚C (a) sample 1 (b) sample 2 and (c) sample 3

Optical properties

The optical property of the ZnO powder at different annealing temperature was studied the physical phenomena and optical constant. The preparation of ZnO powder were analysed by UV absorbance spectra. The absorbance of sample may be influenced by grain size, shape and coverage of sample. Absorbance was checked in wavelength range from 200to1100 nm for different annealing temperature 400°C, 500°C and 600°C. All the samples showed absorption edges around 370 nm which corresponded to the optical band gap of ZnO. The UV spectrum of

Zinc Oxide samples are shown in Figure 5 (a), (b) and (c). From the dependence of the absorption band edge on wavelength, the energy band gap of the material can be determined. To determine the optical band gap, absorption coefficient α of the ZnO film was calculated using,

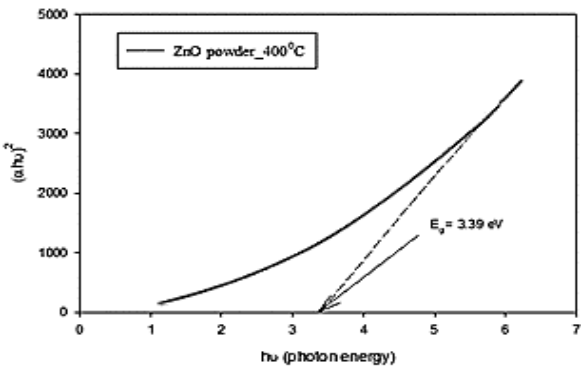
$$\alpha(\gamma) = 2.303\ (A/t)$$

where A is the optical absorbance and tis the thickness of cuvette. The optical band gap of the film was estimated by means of Tauc's equation,

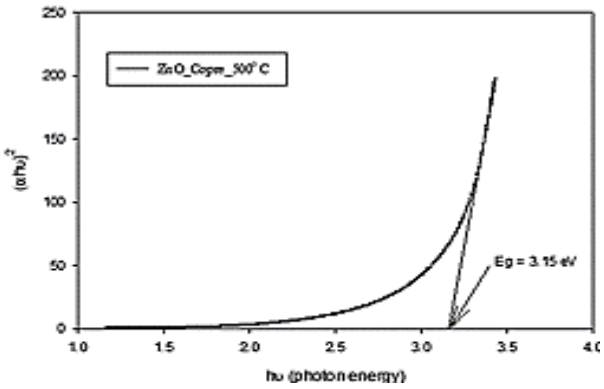
$$(\alpha h\upsilon)^2 = (h\upsilon - E_g)^{1/2}$$

Where hγ is the photon energy and E_g is the optical energy gap. These energy gaps are calculated from the intercept of straight line on the photon energy (hυ) of the $(\alpha h\upsilon)^2$vs (hυ) plot and the value listed in Table 1. The calculated band gap values were 3.15 eV, 3.39 eV and 3.84 eV and treated samples at 400°C, 500°C and 600°C. The UV emission corresponds to near band edge emission due to the fee excitation recombination. The optical band gap of ZnO reduced appreciable with a change in nanoparticle size from 38.15 nm to 41.38 nm as caused by the increase in annealing temperature.

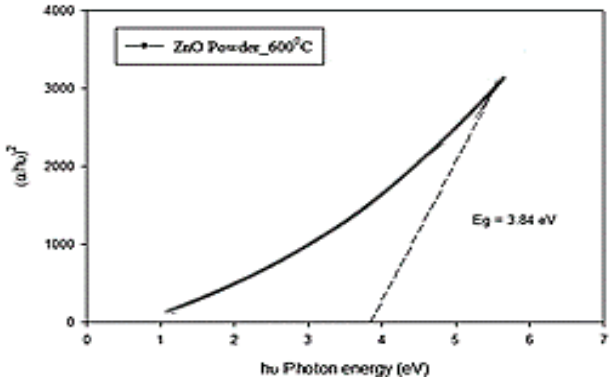
The band gap energy may be attributed to the increase in particle size with increasing annealing temperature as shown by XRD and SEM data. The observed increased in the optical band gap with the increase in annealing temperature could be due to the variation in lattice defects and stress. The annealing process improved the crystallinity, increased the average grain size and band gap energy increased.



(a)sample 1



(b)sample 2



(c) sample 3

Figure 5 Plots of $(\alpha h\upsilon)^2$ vs (hυ) to determine the energy of the optical absorption coefficient for ZnO powder samples with different temperatures
(a) sample 1 (b) sample 2 and (c) sample 3

Conclusion

Zinc Oxide Nano powders by the chemical co-precipitation method and annealed at different temperatures 400°C, 500°C and 600°C. Various properties of ZnO nanostructures have been characterized. The XRD patterns of the samples showed a hexagonal wurtzite crystal structure confirming the synthesis process efficiency. The SEM revealed the formation of agglomerated particles. The research finding, the energy band gap for ZnO was 3.39 eV while the crystallite size 41.38 nm by using UV-vis and XRD. In addition, there was a reaction temperature was important parameter which influences the structural morphology of the particles as well as the particle size. As the reaction temperature was increased there was increased in the particle size. In heating process when the particles are formed, they collide and either coalesce with one another to form a large particle or coagulate. When the temperature was increased, the c/a ratio decreased and the crystallite size increased. The band gap of ZnO powders increased from 3.15to 3.84 eV with an increase in temperature from 400°C to 600°C.The results of this work show that ZnO nanopowders annealed at 500°C is most suitable to make photo electrode which was in a good agreement with the value of optical band gap for ZnO at 3.39 eV and micro strain was the lowest 8.37×10^{-4} because of the dislocation density was found to be 5.84×10^{14} m^{-2}.The results indicate that the ZnO nanopowder prepared by co-precipitation method can be used for solar cell. Then, the samples were characterized by means of XRD, SEM and UV-Vis measurement.

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