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STRUCTURAL, MORPHOLOGICAL AND OPTICAL STUDIES OF ZINC OXIDE (ZnO) THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION TECHNIQUE

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Abstract

In this study, Zinc Oxide (ZnO) thin films have been deposited by chemical bath deposition techniques on Indian Tin Oxide (ITO) glass substrate at 300°C and 400°C. Phase formation and crystal structure of Zinc Oxide thin films were studied by X-ray diffraction (XRD). Results of the Scanning Electron Microscopy (SEM)) were indicated the morphology of the sample surfaces. The optical band gap of Zinc Oxide thin films were studied by absorbent data using UV-Vis Spectrometry.

Keywords : Chemical bath deposition, ZnO, XRD, SEM, UV-Vis

Introduction

Amongst various other semiconducting materials, zinc oxide (ZnO) is widely studied because of its abundance in earth, environmental friendly nature, low cost, wide band gap, large exciton binding energy (60meV) at room temperature, high transmittance in the visible region and excellent thermal and chemical stabilities. Recently ZnO has been recognized as one of the intriguing candidates a wide range of technological applications that include transparent electrodes , piezoelectric, surface acoustic wave filters, photonic crystals, light emitting diodes, photodetectors, optical modulator waveguides, gas sensors, ultaviolet sensor, dye sensitized solar cells, solar cell and photo-catalysts. Many methods have been used to deposit ZnO for various applications. They include ac magnetron sputtering, dc magnetron sputtering, ion implantation, molecular beam epitaxy, metal organic chemical vapor deposition, sol-gel method, spray pyrolysis and chemical bath deposition method. The chemical bath deposition method has an advantage over other methods since it is very simple, it does not require sophisticated equipment, it uses low temperature and has low cost of deposition.

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Chemical Bath Deposition involves deposition of semiconductor thin films on substrates that are kept in the aqueous solutions. This method seems to be more suitable for synthesizing ZnO nanosheet electrodes with a high specific surface area. It has been reported that when ZnO nanosheets were applied in dye-sensitized solar cells, measured electron transport time in these systems was found to be much faster than in comparable mesoporous ZnO films. Together with the high internal surface area and good electrical conductivity, CBD ZnO films offer excellent visible light transmittance. DSSCs has shown that the light harvesting efficiency of film electrodes is influenced by its crystallinity, particle size, surface area, dye affinity, and film porosity. In this paper, thin films of ZnO have been deposited on ITO glass substrate using chemical bath deposition technique. The crystal structure and surface morphology of the film have been studied. The band gap energy and the effect of annealing temperature on band gap energy have also been investigated.

Experimental Procedure

The ZnO deposited onto the ITO substrates were prepared by the chemical bath deposition method at reaction solution temperature at 63.5~80°C. The reaction bath is composed of Zinc chloride ($ZnCl_2$) and Sodium hydroxide (NaOH). An alkali solution of zinc hydroxide was first prepared. Initially, 6.8g of Zinc chloride was dissolved in 50ml of deionized water. After that, it is gradually stirred with magnetic stirrer with 300 rpm and this process at temperature raise to 80ºC. And then 4 g of sodium hydroxide were mixed with 50 ml of deionized water. 25ml of sodium hydroxide solution treated drop by drop without touching to the wall of the container by using burets. The aqueous solution was turned into a milky white collide without any precipitation. The reaction solution was allowed to proceed for nearly two hours after complete addition of sodium hydroxide. After the complete reaction, the Indium Tin Oxide coated glass substrate was immersed vertically at the center of reaction solution in such a way that it should not touch the walls of the beaker. At the end of the deposition period, the observable films were washed with distilled water and drip-dried in air. Post annealing temperature annealing of the films expelled the water molecules resulting Zinc oxide. In this study the annealing temperature were used at 300 ºC and 400 ºC respectively.

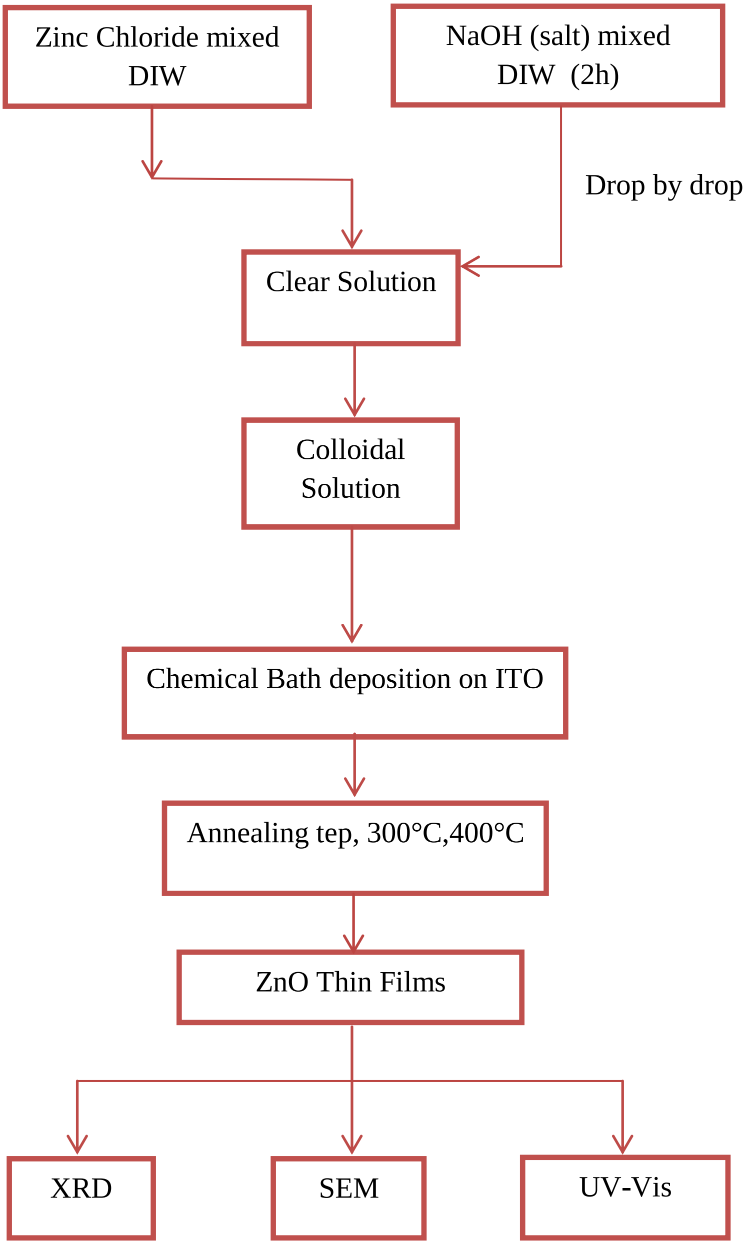

Figure1: Flow chart of preparation of ZnO thin film on ITO glass substrate with different annealing temperatures

Result and Discussion

Structural properties of ZnO thin film by XRD

To examine the crystal structure and phase formation of ZnO/ ITO thin films, they were performed using monochromatic CuKα radiation (λ= 1.54056 Å) operated at tube voltage 40kV and 40 mA (tube current). The X-ray diffraction patterns for zinc oxide thin films were shown in Fig. The upper side of XRD profile was represented the observed profile while the lower side showed the standard ICDD (International centre for Diffraction Data). The comparison between the observed and standard diffraction peal position and relative peak intensities conforms the hexagonal phase for the zinc oxide thin films. Fig 1(a) and (b) show the XRD pattern of the ZnO thin film annealed at 300°C and 400°C for 2h.The patterns of ZnO thin films deposited on ITO substrate revealed three dominant peak at 2ϴ values of32.24°,35.90°and 36.80° corresponding to (100), (002) and (101) plane respectively at 300°C and 32.23°, 35.01° and 37.17° corresponding to (100), (002) and (101) plane respectively at 400°C. The well resolved XRD peaks of the diffraction pattern indicate that the ZnO thin film was well crystallized after the post-reaction annealing treatment. The strong and narrow diffraction peaks indicate that the material has a good crystallite size. The full width at half maximum (FWHM) and crystallites size was calculated using Debye Scherer's formula were given in Table 1, Table 2. The measured lattice parameters (a & c) and lattice distortion c/a for ZnO thin film at different annealing temperature was showed in Table 3.

Morphology and phase analysis of ZnO thin film

The microstructural properties of Zinc oxide thin films deposited onto ITO glass substrate were observed by SEM analysis. The SEM photograph shows nanosheet like structure. The width and thickness of the nanosheets were measured by using well known bar code system. Bar code size was formed to be 2µm with magnification of 5000.SEM images of Zinc oxide thin films on the ITO glass substrate revealed sheet shape distribution some portion of the surface of the substrate. Fig 3(a) showed the SEM image of ZnO film at temperature 300°C and Fig 3(b) provided the sheet shape structure on their film. The average size of nanosheets would be measured by the bar code system and its width were 105.44 nm, 107.11nm and thickness were 2 nm, 3nm at annealing temperature 300°C and 400°C respectively.

Optical Properties of ZnO thin film

The preparation of ZnO thin film, ZnO thin films were characterized by UV absorbance spectra. The optical properties of ZnO film are determined from absorbance measurement in the range of 190nm to 800nm for annealing temperature 300°C and range 190nm to 800nm for annealing temperature 400°C respectively. The maximum absorbance edge was found at 314nm for ZnO thin films for 300°C and 376nm for 400°C annealing temperature. The absorption spectrum of ZnO thin films was shown in figure 4(a) and (b). From the dependence of the absorption band edge on wavelength, the energy gap of the material can be determined. When the energy of the incident photon is greater than that of the band gap ($h\upsilon>E_g$) the absorption coefficient 'α ' is given by

$$\alpha = 2.3026\ A/t \ldots\ldots\ldots\ldots \quad (1)$$

where, t is thickness of the sample

A is the absorbance.

$$\alpha h\mu = A(h\mu - Eg)^{1/2} \text{----------} \ (2)$$

where, A is constant and $h\upsilon$ is the photon energy.

From the curve $\alpha h\upsilon^2$ versus $h\upsilon$, the band gap was identified by extrapolating the linear region of the curve to the energy axis. The energy band gap value of ZnO thin films were measured in figure 5(a) and (b). In these results, the band gap was examined to be 3.960eV and 3.302eV for annealing temperature 300°C and 400°C.

Table1: The structural parameter of ZnO thin film for identified peaks at 300 °C

No.	Peak	FWHM (deg)	2-Theta(deg)	Crystallite size (nm)
1	(1 0 0)	0.092	32.239	93.61
2	(0 0 2)	0.332	35.900	26.28
3	(1 0 1)	0.390	36.800	22.43

Table 2: The structural parameter of ZnO thin film for identified peaks at 400 °C

No.	Peak	FWHM (deg)	2-Theta(deg)	Crystallite size (nm)
1	(1 00)	0.113	32.239	75.53
2	(0 0 2)	0.320	35.005	26.87
3	(1 0 1)	0.577	37.170	14.99

Table 3: Lattice parameters (a & c) and lattice distortion c/a for ZnO thin film at different annealing temperature

Annealing temperature	a(Å)	c(Å)	c/a
At 300^{o}C	3.2068	5.1804	1.6154
At 400^{o}C	3.2047	5.1294	1.6005
Standard	3.2500	5.2000	1.6000

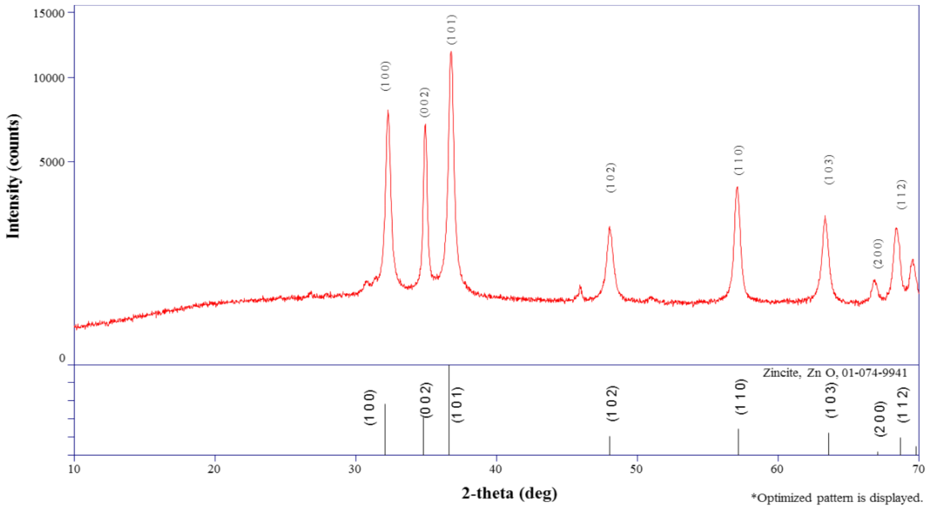

Figure. 2: (a) XRD diffractorgram of ZnO thin film annealed at 300°C

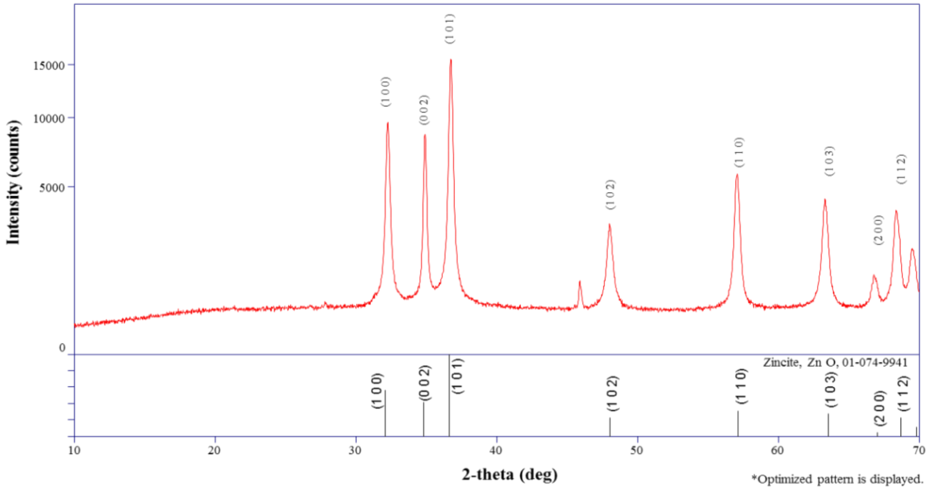

Figure 2: (b) XRD diffractorgram of ZnO thin film annealed at 400°C

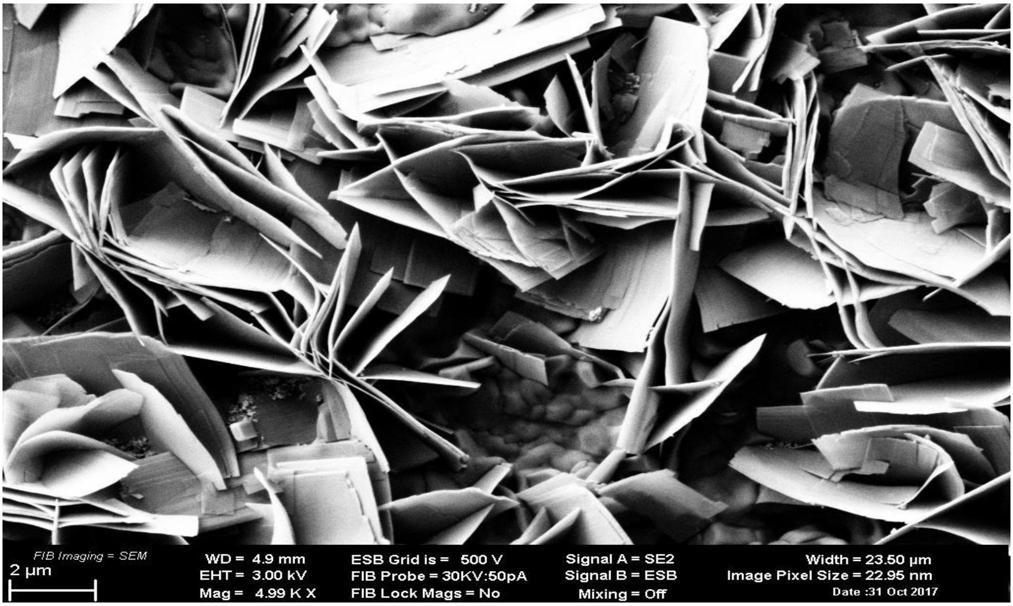

Figure 3: (a) The SEM photograph of the ZnO thin film annealed at 300°C

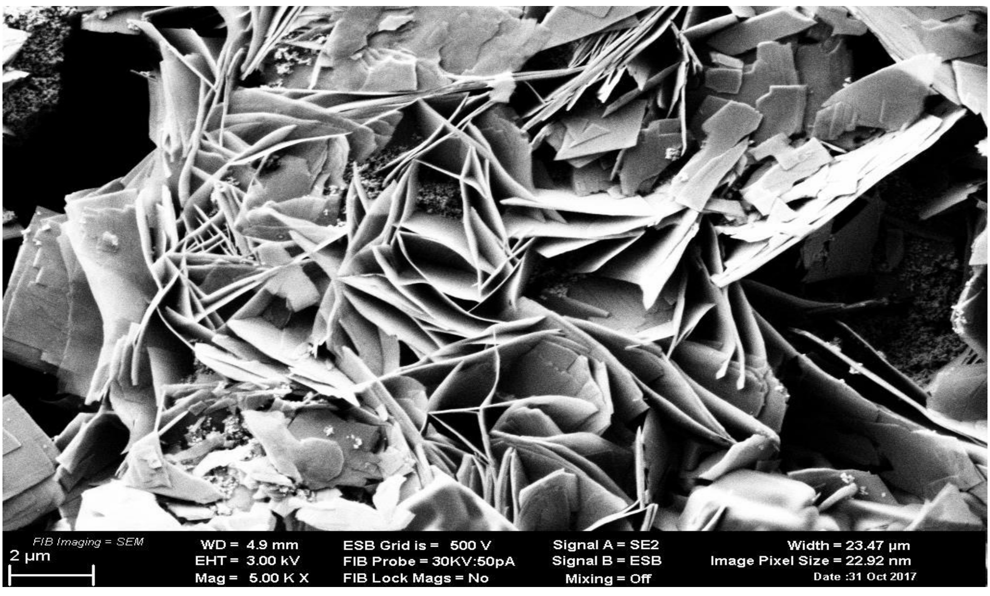

Figure 3:(b) The SEM photograph of the ZnO thin film annealed at 400°C

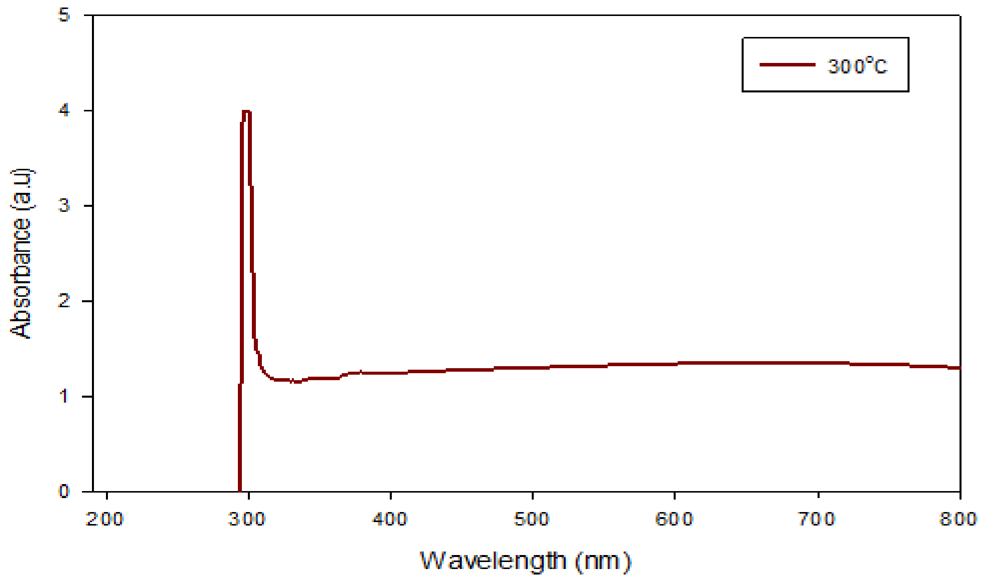

Figure 4: (a) Absorption spectrum of the ZnO thin film annealed at 300°C

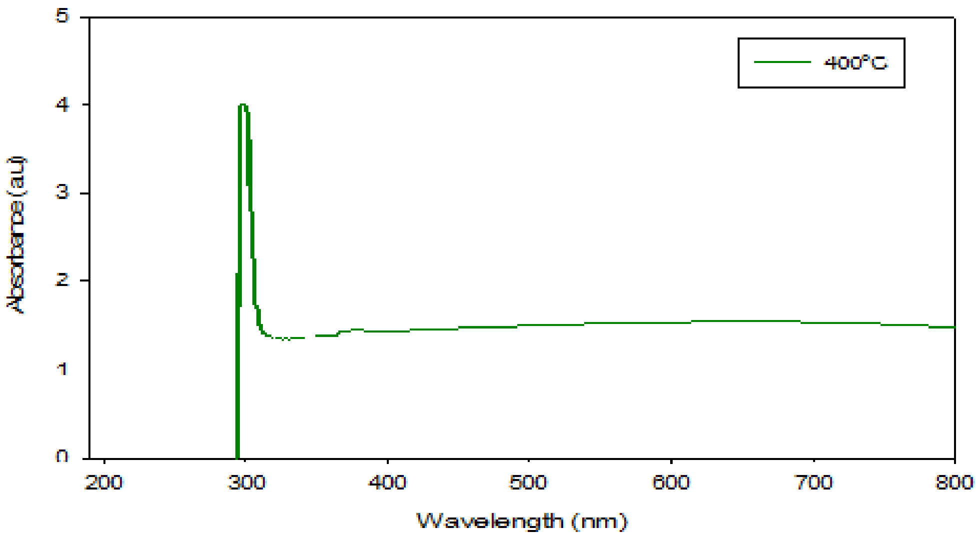

Figure 4: (b) Absorption spectrum of the ZnO thin film annealed at 400°C

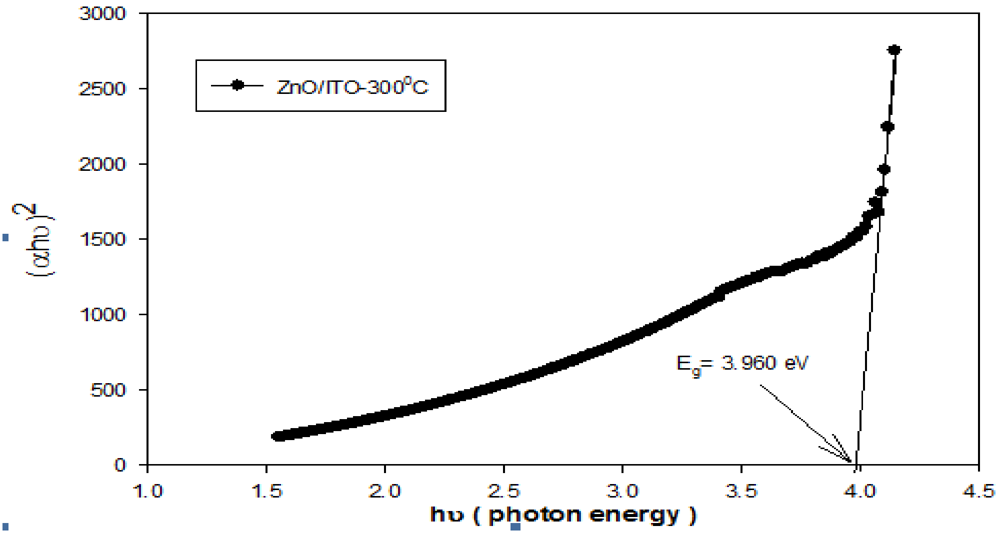

Figure 5: (a) Plot of (αhμ)^{2}versus photon energy of ZnO thin film annealed at 300°C

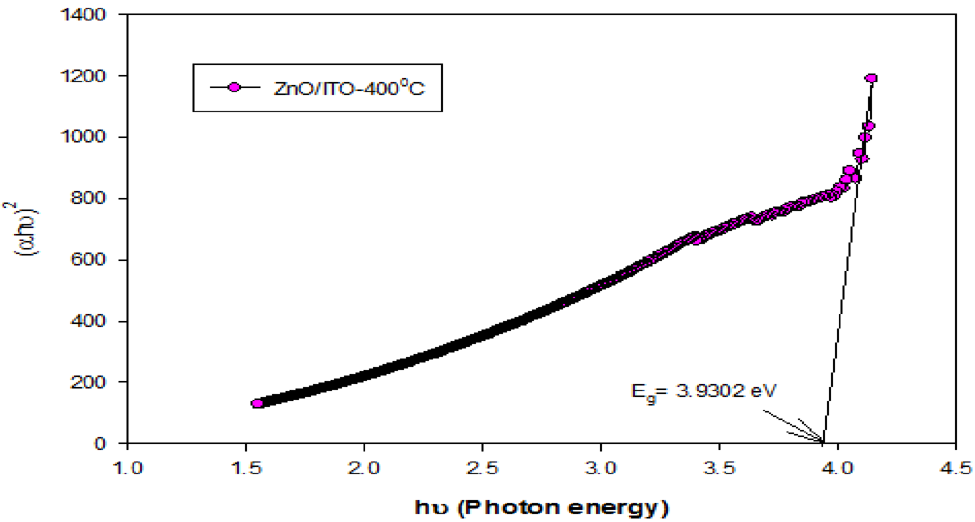

Figure 5: (b) Plot of (αhμ)^2 versus photon energy of ZnO thin film annealed at 400°C

Conclusion

The deposition of ZnO thin films prepared by the successive immersion of ITO glass substrate in solutions of NaOH and Zinc chloride reaction solution at 63.5°C ~80°C have been studied by Chemical Bath Deposition Technique. A sample of CBD technique was developed to synthesize interesting ZnO nanostructures. Hexagonal (wuritze structure) phase can be easily obtained by CBD method. At temperature of 300°C, the crystallite size was found to be 22.43nm at prominent peak (101) and 400°C provided 14.99 nm respectively. Therefore, we may deduce the crystallite size was decreased with increasing annealing temperature. Microstructural of the films changes on varying film precipitation conditions, particularly the annealing temperature. The surface morphology of deposited ZnO thin films on ITO substrate was showed nanosheets structure. The average width of nanosheets would be measured by the bar code system and its width and thickness were105.44 nm, 107.11nm and 2 nm, 3nm annealing temperatureat 300°C and 400°C. Optical band gap of the ZnO thin films, measured by employing a UV –Vis spectrophotometer, lies at 3.960eV and 3.302eV at 300°Cand 400°C annealing temperatures respectively. By the conclusion, the ZnO film is credible and promising use for thin film solar cell by non-expensive and unsophisticated method.

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