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The effect of pH condition on Zinc Oxide growth fabrication using Flexible Substrate

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Abstract
Zinc Oxide (ZnO) nanostructures using glass substrate exhibit attention-grabbing properties together with high chemical process efficiency and robust adsorption ability. Various initiatives have been undertaken to develop ZnO growth on flexible substrates to replace the conventional glass substrate as it can be utilized as flexible optoelectronic and flat panel displays. This research work focused on the effect of pH condition on ZnO growth fabrication using a flexible substrate. In this study, ZnO thin films were deposited on ITO/PET substrate by a spin coating sol-gel method. The precursor solution was prepared by dissolving Zinc Acetate Dihydrate (ZnAc) and Diethanolamine (DEA) in Deionized Water (H2O) and Iso-Propanol (2-PrOH). ZnO thin films were obtained after pre-heating the spin-coated thin films at 100 ℃ for 5 minutes after each coating until five layers obtained. Subsequently, growth solutions were obtained from Hexamethylenetetramine (HMT), Zinc Nitrate-6-Hydrate (ZnN) and Sodium Hydroxide (NaOH), pH adjuster with final solution pH values of 6, 8, 10, 12 and 14. After that, hydrothermal synthesis was done with 90 ℃ for 4 hours. XRD results indicated high intensity on (101) plane, which increased until the optimum pH level of 10 but decreased due to high alkalinity. Meanwhile, FESEM demonstrated hollow nanotube hexagonal wurtzite, nanoneedle-like nanorods, dendrite nanoparticles with nanoflower-like morphology as the pH value increased from 6 to 14. The optical band gap values obtained were in the range of 3.89 to 3.96 eV as pH 10 sample had the highest value. In conclusion, it is proven that the pH condition of the growth solution influences the ZnO growth on ITO/PET substrate.

1.0 Introduction

Zinc oxide (ZnO) has received significant attention due to its distinctive optical, semiconductive, piezoelectric, magnetic and gas sensing properties. ZnO nanostructures exhibit attention-grabbing properties together with high chemical process efficiency and robust adsorption ability (Zhao *et al.*, 2010).

The glass substrate has been widely used with ZnO studies, but it has a drawback on flexibility, weight, and safety matters. Thus, various initiatives have been undertaken to develop ZnO growth on flexible substrates to replace the conventional glass substrate as it can be utilized as flexible optoelectronic and flat panel displays. Indium tin oxide (ITO)

thin film deposited on rigid glass substrates have been typically utilized as transparent carrying out electrodes (Kim *et al.*, 2001).

Many deposition techniques are used to synthesize nanostructures of ZnO like nanowires, nanobelts, nanobridges, nanonails, nanoribbons, nanorods, nanotubes, and nanoflower using thermal evaporation, hydrothermal synthesis, metal-organic chemical vapour deposition (MOCVD), spray pyrolysis, ion beam assisted deposition, laser-ablation, sputter deposition, template assisted growth, chemical vapour deposition and sol-gel method. Among these techniques, the hydrothermal method offers several advantages with excellent control over stoichiometry, composition modification, microstructure control using capping molecules, controlled doping, within costly equipment (Wahab *et al.*, 2009b).

Therefore, we focused on the fabrication of ZnO nanostructures on ITO/PET substrate via the hydrothermal method and investigate the effects of pH condition on the growth of ZnO during formation. The ZnO nanostructures obtained after hydrothermal synthesis with growth solution pH value of 6, 8, 10, 12 and 14 were systematically investigated on the structural, morphology and optical properties.

2. Experimental Methods

In order to do this experiment, an Indium Tin Oxide Coated Polyethylene Terephthalate film (ITO/PET) substrate with surface resistivity of 200 Ω/sq and 0.127 mm of thickness was selected. The substrate was cut into a 2 cm x 2 cm dimension. A blue protecting sheet was removed from the substrate prior to spin coating process and cleaned using acetone and ethanol alternatively with deionized water.

The precursor solution was prepared by dissolving ZnAc and DEA in H2O and 2-PrOH. The molar ratio of ZnAc: DEA: H2O:2-PrOH was 1:1:1:20. The mixture then was stirred by a magnetic stirrer at 70 °C for 2 hours. Precursor solution prepared by this method did not produce any precipitates after two weeks of storage. After overnight ageing, Spin coating via sol-gel process was done with the speed of 500 rpm for 10 seconds followed by 3000 rpm for 30 seconds using VTC-50A Spin Coater. ZnO thin films were obtained after pre-heating the spin-coated thin films at 100 °C for 5 minutes after each coating until five layers obtained.

Then, a growth solution consists of HMT and ZnN was prepared, and NaOH was used to alter the pH value of the solution. Each set of 50 ml growth solution was prepared with varied final pH concentration of 6, 8, 10, 12 and 14 before it was used for the hydrothermal process. The solution was stirred for about 2 h and another 30 min for the NaOH to dissolve well. Synthesis of ZnO was carried out via hydrothermal process in a Carbolite Oven at 90 °C for 4 hours. Afterwards, the samples were rinsed with deionized water and left to dry before characterization.

The crystalline phase of ZnO was characterized using X-ray Diffraction (XRD -Bruker D8) using Cu-Kα radiation in the range of 20° to 80° while the surface morphologies were characterized by field emission scanning electron microscope FESEM (JEOL, JSM 7600F, Japan) at an accelerating voltage of 5 kV after the sample was coated using JEOL, JFC-1600 Auto Fine Coater and Absorbance spectra were

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recorded in the range of 300 to 800 nm by using UV-Vis Spectrophotometer (UV-1800, Shimadzu Corp.). Therefore, five samples of ZnO on ITO/PET substrate were prepared and undergo characterizations process.

3. Result and discussion

3.1 X-ray diffraction analysis

Figure 1 shows the intensity of diffraction peaks was observed at $2\theta = 31.75°$, 34.45°, 36.20°, 47.55°, 56.55°, 62.85° and 68.00° which are related to the respective peaks (100), (002), (101), (102), (110), (103) and (112). The highest diffraction peak can be seen at (101) plane as it indicates nanoparticles formation.

From the diffraction pattern, the pH 6 sample can be indexed as hexagonal wurtzite structures of ZnO, and no peaks for other impurities were detected in the spectra. ZnO rapidly formed and crystalized at samples pH 8 and pH 10 results in its highest peaks in (101) plane as NaOH was added to change the pH condition. The intensity of the diffraction peaks decreased in pH 12 due to the high alkalinity of growth solution. It was also observed that the plane (102) peaks became wider as the NaOH concentration increases because of higher pH value. Finally, the last sample with a pH value of 14 can be seen without any significant intensity of ZnO diffraction peaks because the seed layer is partially worn out at the end of the hydrothermal process.

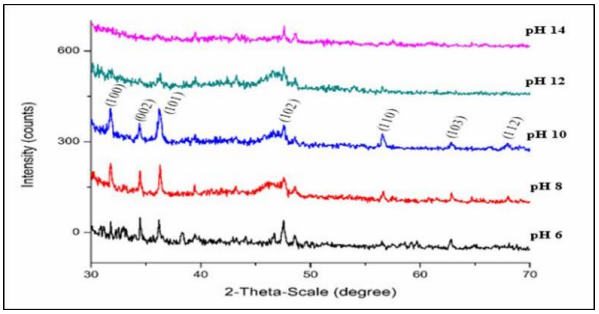

Figure1. XRD pattern for samples varied from pH values of 6, 8, 10, 12 and 14

It can be concluded that the diffraction peak intensity increases until the optimum pH level of 10 with nanoparticles but tend to decrease due to the high alkalinity of the growth solution. The intensity of the diffraction peaks varies with the increasing pH value may be due to the formation of different ZnO nanostructured morphologies, as shown by the FESEM images in the next section.

3.2 Field emission scanning electron microscopy

Figure 2(a) and its insets show the morphology observed at pH 6 sample. It can be noticed that the nanotubes are in a hollow structure with a diameter range of 159 to 389 nm at x100000 magnification. The obtained ZnO hexagonal nanotubes possess a high ratio of volume to the surface which could be very useful in sensing applications, and the intense UV peak also suggests that the material could be employed in photoluminescent according to Raad *et al.*, (2016).

Sample with pH 8 can be observed in figure 2(b) and insets that show nanoneedle-like structure almost similar to findings from Baruah & Dutta, (2009b) using hydrothermal method for pH 8. NaOH added growth solution shows nanorod structure almost formed flower-like structure were observed. Meanwhile, for pH 10 sample in Figure 2(c) shows an organized complete growth of non-homogenous dendritic nanoparticles as it can be correlated with the XRD results obtained for this sample was the highest peak diffraction intensity at (101) plane. It can be observed that the dendrite nanoparticles almost formed a nanoflower-like shape, but the particles are in irregular shapes which

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could be due to a shortage of hydrothermal synthesis duration.

Similarly, non-homogenous dendritic nanoparticles as the former pH 10 sample were observed on sample pH 12, but it was less dense and scattered. ZnO nanoparticle dendrite-like compromised to form nanoflower-like structure can be seen in figure 2(d) and insets. For this sample, the nanostructure grown are very little and scattered compared to previous samples which are due to high alkalinity and seed layer partially worn out in physical observation as shown in figure 2(e). The morphology is noticeably similar to the previous pH 12 sample, which is non-homogenous dendritic nanoparticles that tend to form nanoflower-like structure. Thus, from the sample of pH 10, 12 and 14 it can be distinguished that there is a pattern of ZnO formation declination on the concentration as seen in XRD results that matches the FESEM results as well with decreasing and less dense ZnO growth on ITO/PET substrate surface.

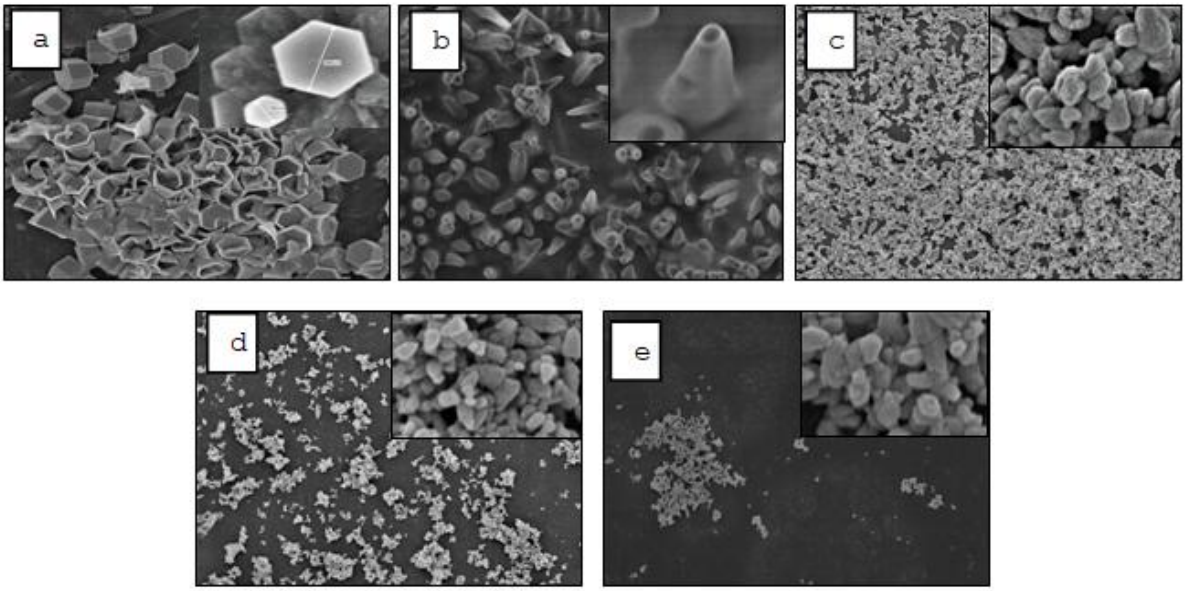

Figure 2. FESEM morphology of ZnO observed and its inset ZnO for (a) pH 6, (b) pH 8 (c) pH 10, (d) pH 12 and (e) pH 14.

This study proves a new experimental variation of result from hollow nanotube, needle-like nanorod and dendrite-like non-homogenous morphology when the pH value increased from pH 6 to 14 in the growth solution. Presumably, pH 10 value is the optimum pH condition for the growth of ZnO on flexible ITO/PET substrate compared to other samples. Therefore, it is highly recommended to increase the hydrothermal process duration because the longer time of application for hydrothermal processes is required to produce a proper formation of nanostructure when using weak alkaline solution (Idris, 2015).

From the above observations, it is evident that the morphological characteristics of the ZnO nanostructures are distinctly controlled by the pH of the growth solution. The results can be related to XRD analysis.

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3.3 UV-Vis Spectrometer

Absorbance testing was conducted to evaluate the optical properties in this study by using a wavelength range between 300 nm to 800 nm. Figure 3 illustrates the absorbance percentage results obtained for the ZnO on ITO/PET substrate with different percentage of optical absorbance.

All samples had a sharp decline in absorbance percentage from the region where the light absorption experience band gap excitation until 320 nm wavelength. A slight drop in the peak can be seen for sample pH 8 and pH 12 at 370 nm and continued a constant slow increasing trend. Meanwhile, sample 14 shows the highest percentage of absorbance among all the samples, which can be correlated to the FESEM results gained. Consequently, the size of the particles influences the ability of ZnO nanoparticles to absorb UV light. The UV-Vis characterization can distinguish that pH 10 sample has the lowest absorbance rate compared to the other samples, which matches the XRD result in the former part of the research. The tail height increases until 800 nm as the pH value increases from 8 to 12, but pH 6 sample showed a stable height until the end.

The optical band gap, Eg of the ZnO on ITO/PET substrate, was determined by extrapolation of the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ plots using the following equation. The following equation was used for the direct transition

$$(\alpha h\nu) = A\,(h\nu - E_g)^{n} \quad (1)$$

where n= ½ for direct bandgap, A is a constant, E_g is the optical bandgap, h is the Planck constant and α is the absorption coefficient. The measured optical band gap values were in the range of 3.89 to 3.96 eV, which is very close to the band gap of ZnO on ITO/PET substrate and are in good agreement with the literature reports. W. Tang *et al.*, (2012) mentioned in his studies that ITO is a wide band gap semiconductor (E_g: 3.5 to 4.3 eV) which shows high transmission in the visible and near-IR regions of the electromagnetic spectrum. Thus, it can be concluded that the bandgap gets better for ZnO on the ITO/PET substrate.

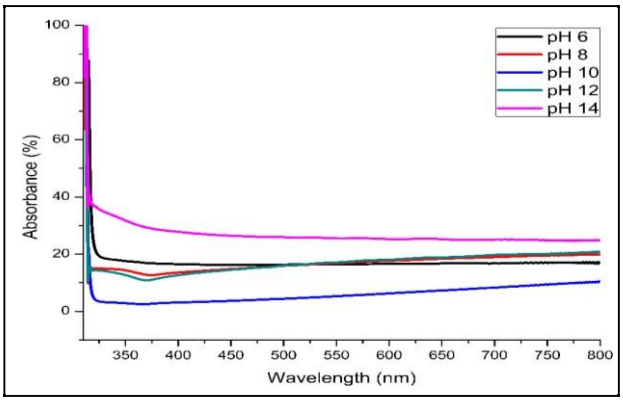

Figure 4. UV–Vis spectra ZnO nanostructures at different pH conditions (pH 6 to 14).

4. Conclusion

Synthesis of ZnO was carried out via hydrothermal process in a Carbolite Oven at 90°C for 4 hours. From this study on the effect of pH variation, it was proven that the structural, morphology and optical properties of ZnO depend on the pH of the growth solution. XRD results indicated high intensity on (101) plane, which increased until the optimum pH level of 10 but eventually decreased due to high alkalinity. Meanwhile, FESEM demonstrated hollow nanotube hexagonal wurtzite, nanoneedle-like nanorods, dendrite nanoparticles with nanoflower-like morphology as the pH value

increased from 6 to 14. The optical band gap values obtained were in the range of 3.89 to 3.96 eV as pH 10 sample had the highest value. Future investigations on the pH variation for ZnO on ITO/PET substrate hydrothermally synthesized using growth solution research is still ongoing.

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