GROWTH OF ZnO NANOSTRUCTURES WITH DIFFERENT ALKALINE PRECURSOR SOLUTION

Ainun Rahmahwati Ainuddin and Wan Nur Amalina Mior Idris
Department of Material and Design Engineering, Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia, Parit Raja, Batu Pahat, Johor, Malaysia
E-Mail: ainun@uthm.edu.my

ABSTRACT
Nanostructures Zinc Oxide (ZnO) are promising candidates for novel application in solar cells, sensors, emerging transistors and optoelectronic devices. ZnO nanostructures have been successfully synthesized by using the hydrothermal technique on Zn substrates at 120 °C. The effect of synthesis condition from different deposition times and pH of alkaline precursor which played a role in the crystallization process were studied by scanning electron microscopy, X-ray diffraction spectra and atomic force microscopy. The I-V characteristic of the ZnO nanostructures were characterized with solar simulator. The results demonstrate that the morphology of ZnO nanostructures are determined by the growth temperature, the overall concentration of the precursors and deposition time. The formation mechanisms of different ZnO morphologies were also investigated based on the experimental results.

Keywords: zinc oxide, hydrothermal, pH, KOH, nanostructure.

INTRODUCTION
Zinc Oxide (ZnO) has a wide number of properties which has gained considerable attention from researchers over the past few years. ZnO is a popular material used in semiconductor research and this was mentioned back in 1945 (Gomez and Tigli, 2012). Worldwide use of ZnO that has 9 % of metallic zinc is more than 1.2 million tonnes per year (International Zinc Association, 2011). Due to its unique chemical properties and structure, ZnO is increasingly being used in the production of electronic devices. The applications of ZnO are not only limited to the engineering field, but also the pharmaceutical industry, cosmetic and food packaging industry (Houng et. al., 2007; Rani et al., 2008).

There are two types of synthesis methods to obtain the ZnO nanostructure. The ways are solution phase synthesis and gas phase synthesis. For solution phase synthesis, normally the aqueous solution is used and the process is referred to as hydrothermal growth process. Baruah and Dutta (2009) in their research said that solution phase synthesis processes consist of several methods; (i) Zinc Acetate Hydrate (ZAH) is derived from nano-colloidal sol-gel route, (ii) ZAH in alcoholic solutions with Sodium Hydroxide (NaOH), (iii) template assisted growth, (iv) spray pyrolysis for growth of thin films, and (v) electrophoresis. Due to the variety in methods, the structure and look of ZnO produced could be different. The best structure of ZnO is nanowire because of its good performance in electronics, optics and photons field (Zhang et al., 2012). Hydrothermal synthesis is a robust and economic method for the growth ZnO nanowires that can be carried out with simple equipment unlike the other methods mentioned (Akgun et al., 2012; Tong et al., 2006; Liu et al., 2005).

The properties of zinc oxide strongly depend on the synthesis method and conditions during processing. It is therefore critically important to develop synthetic strategies that control both size and shape while at the same time yielding materials with well-defined compositions and structural morphologies. Moreover, the size and shape of the structures grown by this synthesis can be controlled by adjusting the growth parameters such as concentration of solution, reagents stoichiometry, temperature and pH (Sambath et al., 2012; Pei et al., 2010).

In this work, we focused on the fabrication of ZnO nanostructures via hydrothermal synthesis and the effects of alkaline solution on the morphologies. The ZnO nanostructures obtained after hydrothermal deposition of 6, 12 and 24h were produced in order to systematically investigate the effect of prolonged growth time on the structural and crystallinity by varying pH.

MATERIAL AND METHODS
Zinc foils (10 mm × 10 mm × 0.5 mm), used as both a solid reagent and as substrates for the direct growth of nanostructured ZnO films, were carefully cleaned in acetone containing ultrasound baths for 20 minutes. Prior to hydrothermal deposition the Zn foils were chemically etch using hydrochloric acid (HCl) in ethanol (EtOH) for 3 minutes. Purpose of etching process was to remove unwanted substances from the foils.

Concurrently, potassium hydroxide (KOH) (Kanto Chemical, 99%)solution was added with deionized (DI) water to form precursor solution until the pH values were 10 and 12. The precursor solutions were put in Teflon-lined stainless steel autoclaves and the clean Zn foils were added to each solution. The autoclaves were tightly closed, heated at 120 °C for 6, 12 and 24 h before left to cool down to room temperature. The as-synthesized films on Zn substrates were rinsed with DI water several times and dried at 60 °C for 3 h.

The crystallinity and phases of the ZnO nanostructures were characterized by an X-ray diffractometer (XRD, PANalytical XPert Powder) using Cu-Kα radiation in the range of 20 to 80°while the surface morphologies were characterized by field emission scanning electron microscope (FE-SEM, JEOL JSM-
7600F) and atomic force microscope (AFM, Park Systems XE-100). The solar simulator (Newport type Sol 1A) was used to obtain the I-V characteristic of the ZnO nanostructured.

RESULTS AND DISCUSSIONS

Morphology and the structure of the hydrothermally derived ZnO nanostructures

The low magnification SEM images and their inserts as high magnification images of the ZnO nanostructures synthesized at the pH values of 10 and 12 at increasing deposition time were presented in Figure-1. Figure-1 also shows the different morphologies of the ZnO on Zn substrates. In this research, pencil-like, nano wire sand nano rods ZnO were synthesized in KOH alkaline solution.

After 6 h of hydrothermal exposure in pH 10, pencil-like ZnO nanorods were observed from the surface morphology as shown in Figure-1(a). After 24 h of hydrothermal reaction, the average diameter of the nanorods decreased to form nanowires as shown in Figure-1(b). Increasing the pH value to 12, the ZnO nanostructures are observed as obelisk shaped ZnO nanorods as shown in Figure-1(c). Finally in Figure-1(d), further increase in hydrothermal reaction of pH value 12, a blunt tip of multiple layered crystal structure of obelisk shaped ZnO nanorods occurred. Similar ZnO nanostructures also observed by other researcher in their synthesized (Li et al., 2007; Wang et al., 2004; Sambath et al., 2012; Alias et al., 2010).

From the above observations, it is obvious that the morphological characteristics of the ZnO nanostructures are distinctly controlled by the pH of the precursor and the deposition time. It was observed that the thickness and morphology of the ZnO nanorod arrays are affected by the alkalinity of the solution in the growth bath. The results can be related to AFM analysis.

Surface roughness of ZnO nanostructures were analyzed by AFM. Among the information that can be obtained from surface roughness analysis are average surface roughness (Ra) and root mean square roughness (Rq). Figure-2 shows the surface topologies of ZnO films with different pH values and deposition time by AFM measurements.

Scans of the few areas on the ZnO nanostructures surface shows the root mean square (RMS) roughness(Rq) were 286, 262 and 189 nm for pH value 10, while 98.32, 92.09 and 91.83 nm for pH value 12 with increasing deposition time from 6, 12 and 24 h, respectively. Based on the above RMS values, the surface roughness of KOH

![Figure-1. SEM images of ZnO nanostructures synthesized in KOH of (a) pH 10, 6 h; (b) ph 10, 24 h; (c) pH 12, 6 h and (d) pH 12 24 h deposition time.](image-url)
samples decreased due to the increase of pH value and hydrothermal process hours. There was a big difference in values of surface roughness for pH 10 and pH 12. The value of $R_q$ for pH 12 was less than 100 nm compared to $R_q$ values for pH 10. The surface morphology shows larger grains with the increase of pH value. This statement is supported by research conducted by Sagar et al. (2007).

The variation intensity of the diffraction peaks with the increasing pH and deposition time may be due to the formation of different ZnO nanostructured morphologies as shown by the SEM images. The absence of other peaks clearly suggests the formation of single phase ZnO. The strongest peak corresponds to the 101 plane is more prevalent for the nanostructures as reported by Sambath et al. (2012).

To calculate the grain sizes of ZnO nanostructures, D values which are related to the crystallite size were calculated according to the Scherrer from equation (1):

$$D = \frac{K\lambda}{B\cos\theta}$$  

(1)

Where $K$ = shape factor constant (0.9), $\lambda$ = wavelength of the x-ray (1.5405600), $\cos\theta$ = cosine of half the 2θ angle, and $B$ = broadening of diffraction line measured at half its maximum intensity (radians).

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The grain size of ZnO nanostructures are found to be 41.6, 42.5, 48.5, 41.6, 44.8 and 45.8 nm for pH value 10 and 12 with deposition time of 6, 12 and 24 h, respectively. The average size is calculated using Scherer formula. The improvement in grain size is in conformity with AFM results, where the morphology shows larger grains with the increase of pH (Sagar et al., 2007).

**Current against voltage measurement**

The nanostructure of ZnO was analyzed using a 2-point probe equipment to measure the current against voltage. From the results of the voltage and current, the resistivity can be ascertained. Resistivity can be calculated from the value of voltage and current. Table-1 shows the

![Figure-2. AFM images of ZnO nanostructures synthesized at (a) pH 10, 6 h; (b) pH 10, 12 h; (c) pH 10, 24 h; (d) pH 12, 6 h; (e) pH 12, 12 h and (f) pH 12, 24 h deposition time.](image)

![Figure-3. X-ray diffraction pattern of ZnO nanostructures prepared at (a) pH 10, 6 h; (b) pH 10, 12 h; (c) pH 10, 24 h; (d) pH 12, 6 h; (e) pH 12, 12 h and (f) pH 12, 24 h deposition time.](image)
value of voltage, current, and resistivity for all ZnO samples that underwent the hydrothermal process.

Based on the previous study from Shariffudin et al., (2012), resistivity is closely related with the film thickness which is the thickness of ZnO layer that grow on the surface. The resistivity will increase with increasing film thickness. Besides that, the increased resistivity on ZnO thin film is caused by the porosity of the thin film. Hong et al., (2013) found that increasing porosity decreases the electrical conductivity of ZnO. The higher the porosity occurring on ZnO nanostructures, the higher the resistivity.

Table-1. Results for the electrical properties of ZnO nanostructured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voc (V)</th>
<th>Isc (A)</th>
<th>Resistivity, $\rho$(\Omega m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (pH10, 6 h)</td>
<td>0.02233</td>
<td>0.00136</td>
<td>0.16419</td>
</tr>
<tr>
<td>b (pH 10,12 h)</td>
<td>0.00832</td>
<td>0.00011</td>
<td>0.75636</td>
</tr>
<tr>
<td>c (pH10, 24 h)</td>
<td>0.00263</td>
<td>0.00004</td>
<td>0.65750</td>
</tr>
<tr>
<td>d (pH12, 6 h)</td>
<td>0.00482</td>
<td>0.00002</td>
<td>2.4100</td>
</tr>
<tr>
<td>e (pH 12, 12 h)</td>
<td>0.00585</td>
<td>0.00004</td>
<td>1.4625</td>
</tr>
<tr>
<td>f (pH12, 24 h)</td>
<td>0.00841</td>
<td>0.00006</td>
<td>1.40167</td>
</tr>
</tbody>
</table>

Based on the SEM images in Figure-1, the porosity on the ZnO nanostructures can be seen clearly. This clearly shows that the porosity in samples influenced the resistivity of this sample.

CONCLUSIONS
Based on the study done on pure Zn foil, it is proven that parameters such as the duration for hydrothermal process, types and the pH concentration of alkaline solutions are able to influence the characteristics of ZnO nanostructures. The use of alkaline solutions greatly affected the growth of ZnO nanostructures. The longer time of application for hydrothermal processes is required to produce a good formation of nanostructure when using weak alkaline solution as a precursor. Higher values of pH solutions were used to help the ZnO layer growth on Zn foils. Using hydrothermal synthesis, the production of ZnO becomes more environmentally friendly.

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REFERENCES


