Hydrothermal growth of ZnO: a substrate-dependent study on nanostructures formation

N U Saidin\textsuperscript{a}, T F Choo\textsuperscript{b} and K Y Kok\textsuperscript{c}

Materials Technology Group, Industrial Technology Division, Malaysian Nuclear Agency, Bangi 43000 Kajang, Selangor, Malaysia

\textsuperscript{a}ubaidah@nm.gov.my
\textsuperscript{b}ctfoo@nm.gov.my
\textsuperscript{c}kyk1000@nm.gov.my

Abstract. ZnO has received lots of attention in recent years because of its unique properties, rendering it a good candidate material for various industrial applications. Amongst the methods used for synthesizing ZnO structures, hydrothermal technique offers a simple, cost-effective and yet environment friendly synthesis route for the materials. To investigate the effect of substrate on the formation of hydrothermally grown ZnO, several types of substrates were used and the structures of the ZnO were systematically studied by field emission scanning electron microscopy (FESEM). It was demonstrated that the type of substrates used had a great influence on the morphologies, density and alignment of the ZnO formed. Pre-coated substrate with Au yielded highly aligned ZnO nanorod arrays compared to bare Si and Al substrates. Possible mechanisms for the variation of morphology obtained are discussed.

1. Introduction

Zinc oxide (ZnO) possesses unique chemical and physical properties such as wide band gap (3.37 eV at room temperature) and high-exciton binding energy. This II-VI semiconductor is of great interest for a wide range of applications including sensors [1], light emitting diodes [2], solar cells [3], photocatalysts [4] and others.

Previous research has shown that the properties of ZnO depend strongly on its microstructures. To date, many forms of ZnO nanostructures have been reported, for instance tubes, spheres, wires, belts, helices, plates, islands, boxes, walls, rods, and flakes. These structures are affected by processing parameters like the synthesis method used, type of substrate, synthesis temperature and others. Various methods on the synthesis of ZnO have been reported in the literatures: chemical vapor deposition [5], magnetron sputtering deposition [6], pulsed laser deposition [7], electrochemical deposition [8] and hydrothermal method [9]. Hydrothermal method has become one of the favorite techniques in the growth of ZnO because, besides requiring moderate synthesis temperature, it is low-cost, simple and environmental friendly [10, 11].

Normally for hydrothermal method, a seed layer of ZnO nanocrystals is required to provide the homoepitaxial nucleation sites. This seed layer is generally prepared by sol-gel, sputtering, spin coating or physical vapor deposition techniques. This is followed by annealing process to ensure that the seed particles are successfully formed and adhered to the substrate [12]. However, the use of high temperature for annealing is detrimental to hydrothermal growth. The seedless approach, on the other
hand, requires expensive substrates such as GaN or external electrical field to enhance ZnO growth [11]. To overcome this, the growth of ZnO can be performed via seedless hydrothermal technique assisted by galvanic process on different types of substrates. Zheng et al. (2013) demonstrated that the growth process could be performed on different conducting materials substrates [11]. In this work, we adopted this method for the synthesis of ZnO on different substrates, namely silicon (Si) wafer, gold (Au)-coated Si wafer, aluminum (Al) wire mesh and Au-coated Al wire mesh. A systematic study on the morphological changes of ZnO structures on these substrates was carried out.

2. Experimental
All chemicals in this work were of analytical grade and used as received without further purification. The synthesis of ZnO by the galvanic hydrothermal technique has been reported in our previous work [13]. In this work, the substrates used were Si wafer, Au-coated Si wafer, Al wire mesh and Au-coated Al wire mesh. The Si wafers were cut into a dimension measuring 1 cm × 2 cm while the Al wire meshes were cut into the size of 2 cm × 2 cm. All substrates were first rinsed ultrasonically in acetone, ethanol, isopropanol and distilled water for 15 min successively. The edges of the substrates were then wrapped around with Al foils. An aqueous solution containing 25 mM zinc nitrate hexahydrate ($\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$) and 25 mM hexamethylenetetramine (HTMA C$_6$H$_{12}$N$_4$) was used as the electrolyte. The solution was maintained at 75 ºC on a hotplate and the growth time for ZnO was 4 h. After reaction, all the samples were taken out of the electrolyte and rinsed with deionized water for several times. The morphologies and microstructures of the ZnO were characterized by a field emission scanning electron microscopy (FESEM, GeminiSEM 500, Carl Zeiss). Figure 1 shows the schematics of the experimental set-up.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Schematics of the experimental set-up: (a) edges of the substrate were covered with an Al foil and (b) the substrate was floated down-face on the solution

3. Results and discussion
In this study, zinc nitrate was used as the $\text{Zn}^{2+}$ precursor and HMTA as a weak base and pH buffer. ZnO was synthesized based on the following chemical reactions [10, 12]:

- **Decomposition reaction:**
  \[(\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 6\text{HCHO} + 4\text{NH}_3\]  

- **Hydroxyl supply reaction:**
  \[\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-\]  

- **Supersaturation and ZnO growth reaction:**
  \[\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}\]
It is generally accepted that HMTA decomposes slowly in a heated aqueous solution to yield ammonia and formaldehyde as the initial reactants, which in turn resulting in the formation of hydroxide ions (Eq. 1-2). The hydroxide ions further reacts with the Zn\(^{2+}\) to form zinc complexes which finally transforms into ZnO.

For galvanic-based hydrothermal method, the growth mechanism is similar to that of the electrochemical deposition, except that a galvanic cell is employed instead of using the external power source. Difference in the work functions between Al (sacrificing anode) and the substrate (cathode) provides the bias to drive electrons from Al to the substrate. In this method, Al atoms lose electrons to develop positive charges and the electrons are transferred to the substrate that acts as a cathode. At the cathode, reduction process occurs in which oxygen is dissolved. This is followed by the formation of zinc hydroxide, Zn(OH)\(_2\) which then undergoes dehydration to form ZnO as shown in Eq. 4-6 [13]:

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- & \rightarrow 4\text{OH}^- \quad (4) \\
\text{Zn}^{2+} + 2\text{OH}^- & \rightarrow \text{Zn(OH)}_2 \quad (5) \\
\text{Zn(OH)}_2 & \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (6)
\end{align*}
\]

Figures 2-5 display the FESEM images of the samples. Different substrates used produced different morphologies of ZnO structures. When bare Si wafer was used as the substrate, flower-like ZnO morphology was obtained. These flower-like structures were assembled from many rod structures with average length of 2.9 \(\mu\)m. On close examinations, the structures reveal that each single rod was hexagonal in shape with average diameter of \(\sim598\) nm in size (Figure 2a-b). However, when Au-coated Si wafer was used, aligned ZnO nanorods of pencil-like structure with average diameter of 1.8 \(\mu\)m were grown perpendicularly to the substrate surface (Figure 3a-b).

![Figure 2](image-url)

Figure 2. (a) FESEM images of ZnO nanorods grown on bare Si wafer (a) side-view and (b) top-view. Inset shows that the rod is hexagonal in shape
Figure 3. (a) FESEM images of ZnO nanorods grown on Au-coated Si wafer (a) side-view and (b) top-view. Inset shows that the rods are pencil-like in shape. When bare Al wire mesh was used as the substrate, randomly interconnected ZnO microflakes covered with nanorods were obtained (Figure 4). In contrast, the Au-coated Al wire mesh substrate produced uniform arrays of ZnO nanoflowers. This suggests that galvanic reaction helps to promote ZnO growth in nanorod shapes (Figure 5 a-b).

Table 1 simplifies various growth structures of the ZnO obtained with different types of substrates:

| Substrate       | Structures          |
|-----------------|---------------------|
|                 |                     |

Figure 4. (a) FESEM images of ZnO nanorods grown on bare Al wire mesh (a) side-view and (b) top-view

Figure 5. (a) FESEM images of ZnO nanorods grown on Au-coated Al wire mesh (a) side-view and (b) top-view
4. Conclusions
Distinct morphologies for the ZnO growth can be achieved on different substrates using seedless galvanic assisted hydrothermal method. ZnO growth on Au-coated Si wafer exhibits well-aligned pencil-shaped rod-like structures while others produced flower-shaped rod structures.
5. References

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