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## Influence of Growth Time and Temperature on the Morphology of ZnO Nanorods via Hydrothermal

Syahirah Shaziman, Ahmad Syakirin Ismail@rosdi, Mohamad Hafiz Mamat, Ahmad Sabirin Zoolfakar

Faculty of Electrical Engineering, MARA University of Technology, 40450 Shah Alam, Selangor, Malaysia.

Emails: ahmad074@salam.uitm.edu.my

Abstract. This research investigates the effect of temperature and growth duration on the morphology of ZnO. ZnO nanostructure can be synthesized via hydrothermal method using Zinc Acetate and hexamethylenetetramine (HMT) as precursor and glass slide as a substrate. The temperature and growth time vary from 50-95°C and 50-100 minutes, respectively. The substrates with ZnO nanostructures are annealed at different temperatures which are 200°C and 500°C. The result indicates that different temperature and growth time produces different morphologies in size. Thus, the morphology of ZnO nanostructure affects by the parameters such as temperature and growth time via hydrothermal grown.

#### 1. Introduction

Zinc oxide (ZnO) is frequently used in several areas of technology due to its unique properties such as large excitation binding energy of 60meV direct wide band gap (Eg~3.3 eV at 300 K) which is widely used for production of green, blue-ultraviolet, and white light-emitting devices [1] and can be effectively grown at low temperature (less than 700 C) [1]. Related to the remarkable features and has large surface-to-volume ratio of ZnO nanostructures [2], it has been widely used in various applications, such as solar cells[3], photocatalysts [4], memristor[5], gas sensors[6] and piezoelectric devices [7].

The properties of such materials of ZnO nanostructures are strongly dependent on their microstructures [8], including crystal size, specific surface [9] and especially on morphologies [10]. Different application may need different types of ZnO nanostructure, size, shape, morphology and growth orientation [2]. There are several types of dimensions in ZnO such as dimensional (1D), twodimensional (2D) and three-dimensional (3D) ZnO nanostructures. However, most of the researches are mainly focused on one-dimensional ZnO nanostructures, such as nanowires, nanorods and nanotubes[11] due to its unique features such as less grain boundary, surface defect, and dislocation [12]. These nanostructures can be synthesized through various techniques. The synthesis techniques include thermal evaporation[13], chemical vapour deposition (CVD) [14], physical vapour deposition[15], hydrothermal[16], sol-gel [17], and electrochemical deposition [18]. However hydrothermal synthesis is chosen as the best method among these because of its low-temperature (60-100 C), low cost, high yield [19,20] and the growth parameters are much easily controlled the shape and dimension of ZnO nanostructures, compared to other techniques[21,22].

There are several parameters that affect the morphology of ZnO nanostructures in hydrothermal synthesis. Mudan Wang et al.[23] studied that parameters such as seed layer, ZnO colloid concentration, substrate, and precursor concentration are hardly effect on the alignment of ZnO nanorods array. In this study, it clearly shown that different sizes of ZnO nanorods can be obtained by manipulating all these parameters. Thus, this research investigates the effect of time and temperature on the morphology of ZnO nanorods via hydrothermal method.

#### 2. Methodology

#### 2.1. A. Preparation of ZnO seed layers

Glass slides were cleaned by using acetone, ethanol and distilled water. The seed layer was prepared by mixing solution of Zn Acetate (CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O , 0.4 M), Aluminium Nitrate Nanohydrate (Al(NO<sub>3</sub>)<sub>2</sub>) and Monoethanol Amine(C<sub>2</sub>H<sub>7</sub>NO) in 2- methyoxyethanol (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>). The prepared solution was stirred and heated at 250 rpm and 80 C, respectively for 3 hours. It was continuously stirred on the hot plate without heating for 24 hours. The solution was then spin coated on glass substrate at 2500 rpm for 1 minute. The coated substrate was annealed at 200 C for 10 minutes to obtain ZnO seed layer. The spin-coating method was repeated for 5 times to obtain the surface thickness on the substrate. The coated glasses were post annealed at 500 °C for 1 hour to introduce nucleation sites that give contribution for absorbing zinc nutrients during the growth process and for forming nanorods [2].

#### 2.2. Growth of ZnO nanorods via hydrothermal method

7.01 g of hexamethylenetetramine (HMT)( $C_6H_{12}N_4, 0.1M$ ) solution will be mixed with Zn Nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>,0.1M). Both of the solutions were immersed in ultrasonic bath for 30 minutes. The precursor was stirred well on a hot plate for 3 hours. The glass slides coated with the annealed seed layer which act as a substrate was immersed in the precursor and heated at C for 50 and 80 minutes respectively to study the effect of ZnO at different growth time. After 50 and 80 minutes, the substrates were rinsed with deionized water. However, the same procedure was carried out for at 95 C to investigate the effect of temperature on the morphology of ZnO nanorods. The substrates with ZnO nanorods were dried at 1 C for 10 minutes and post-annealed with different temperature at 200 and °C for 1 hour. The morphology of ZnO nanorods were observed by FESEM images.

#### 3. RESULT AND DISCUSSION

#### 3.1 Effect of growth time on ZnO nanorods

In the formation of ZnO nanorods, thin film ZnO seed layer is required to promote the epitaxial nucleation on the glass substrate [24]. Fig. 1 shows the effect of growth time on the size of nanorods at different annealing temperature. Based on the Fig. 1(a), at immersion and post-annealing temperature at 80 °C and 95 °C, respectively, the size of nanorods increases from 46.25 nm to 162.50nm as the growth time increases from 50 to 80 minutes. Overall, it can be observed that the size of nanorods increase as the growth rate increases at fixed immersion temperature.

Theoretically, the chemical reaction of the formation of ZnO nanorods can be summarized as below [10,25,26]

$$(CH)_6N_4 + 6H_2O \rightarrow 6HCHO + NH_3$$
(1)

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$
 (2)

$$Zn^{2+} + NH_3 \rightarrow Zn NH_3)_4^{2+}$$
(3)

$$\operatorname{Zn}^{2+} + 4\operatorname{OH}^{-} \to \operatorname{Zn}(\operatorname{OH})_{4}^{2-}$$
 (4)

$$Zn(NH_3)_4^{2+} + 2OH^{-} \rightarrow ZnO + 4NH_3 + H_2O$$
 (5)

$$Zn(OH)_4^2 \rightarrow ZnO + H_2O + 2OH^2$$
 (6)

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In the initial growth of ZnO nanorods, the HMT begins to decompose into ammonia (Eqs.(1)) and provide the hydroxide ions, OH<sup>-</sup> (Eqs.(2)) [10]. The Zn<sup>2+</sup> cation further reacts with NH<sub>3</sub> and OH<sup>-</sup> anion to form ZnO nuclei (Eqs.(3) and Eqs.(4)) [25]. The formed crystal nuclei will grow, and then degraded into ZnO nanorods nuclei with the influence of more OH ions under a certain temperature according to Eqs. (5) and (6) [25]. Hence, as the time increases, the ZnO nuclei will continuously growing. Zn on the surface of the Zn substrate is further oxidized from the oxygen to form ZnO nanorods on the substrate [27]. While Zn atoms attached to the ZnO nuclei edges, the oxidization process causes lateral growth of ZnO nuclei [28,29]. Based on the Fig. 1(b), at the immersion and post-annealing temperature of 95 °C and 500 °C, repectively, the size of nanorods decreases from 62.50 to 56.25. Hence, the ZnO nanorods may grow on the top of other layer of nanorods. This may due to the continuous consumption of Zn nanorods [30].

Shuzi Li *et al* demonstrates that there are many small ZnO rods at the bottom of each ZnO hexagonal structure, this phenomenon means that the ZnO crystallite rods amalgamate each other at the later growth stage because the growth velocity of ZnO is faster along the c axis than that of other directions[31]. Based on the Fig. 2 (e) and (g), it can be observed that the densitiy of nanorods decreases as the temperature increases at the immersion temperature at 95 °C. This is a spontaneous process that occurs because larger crystals are more energetically favoured than smaller crystals[33]. In this case, kinetically favoured tiny crystallites nucleate first in supersaturated medium and are followed by the growth of larger particles (thermodynamically favoured) due to the energy difference between large and smaller particles of higher solubility based on the Gibbs-Thomson Law [34]



Fig. 1 Effect of growth time on ZnO nanorods at immersion temperature (a) 80 °C and (b)95 °C

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Fig. 2 FESEM images of ZnO nanorods were annealed at different immersion time and growth at different time at different annealing temperature (a-d) 80 °C, (a-b) and (c-d) growth for 50 and 80 minutes;(e-h) 95 °C,(e-f) and (g-h) growth for 50 and 80 minutes

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#### **3.2** Effect of immersion temperature on ZnO nanorods

Based on Fig. 2, the size of nanorods decreases when the immersion temperature increases. The length of nanorods is expected to be increased as the temperature increases. Based on the comparison between Fig. 2 (c)-(d) and (g)-(h), it shows that ZnO nanorods grow less densely packed as the temperature increases. This can be explained by that the increasing of reaction temperature that will enhanced the aggregation of the ZnO nanorods as well as accelerates the collision between nucleation atoms during the ZnO hydrothermal process [35]. This kind of collision may cause the dispersion and desorption of nucleation atoms, which reduces the probability for tight aggregation of the ZnO nanorods [35,36]. However, when the growth time is at 50 minutes with annealing temperature at 200 °C, the size increases from 46.25 to 68.75 nm. Increasing in temperature may due to nucleation atoms acquire enough thermal energy at a higher solution temperature which quickly elevates their surface mobility and makes them become more activated [37].

#### 3.3. Effect of annealing temperature on ZnO nanorods

Based on the Fig. 1 and 3, it shows that the microstructures of ZnO nanorods change at a higher annealing temperature as the movement of atom increases [38]. However, it is observed that the size of nanorods is bigger at the annealing temperature of 200 °C than 500 °C. The ZnO nanorods at a higher annealing temperature has lesser crystallinity than the lower annealing temperature. It may occur due to the weak stability of glass that affects the stability and recrystallization of ZnO nanorods at a higher temperature[38]. The further increase of the annealing temperature may induce the desorption of ZnO from the substrate[38]. It is also accepted that as the temperature increases to higher, the movements of molecules become more violent as the annealing temperature is higher [39]. This will deteriorate the perfection of crystal lattice [39].



Fig 3 Effect of immersion temperature on ZnO nanorods at growth time (a) 50 minutes (b) 80 minutes

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#### 4. Conclusions

The effects of growth time and temperature on the morphology of ZnO nanorods have been successfully investigated. The ZnO nanorods are formed on the ZnO seed layers. As the growth time increases, the size of nanorods. However, the size of nanorods decreases at annealing and immersion temperature at 500 °C and 95 °C, respectively. The size of nanorods decreases as the immersion temperature increases. At the fixed growth time at 50 minutes, the size of nanorods increases at annealing temperature of 200 °C. It shows that different growth time and temperature gives a big impact on the size of nanorods. In addition, the size of nanorods is also affected by the post-annealed temperature at 200 C and 500 °C. Overall, the higher temperature results in smaller size of nanorods. The obtained results were characterized by FESEM.

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