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Hydrothermal Growth Route of ZnO Nanorods for Use in Thin Film Solar Cell Devices

[1] W. A. Dhafina, 2 E. A. Ghapur, [3] S. Hasiah
[1] Department of Physical Science, Faculty of Science & Technology, University Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.
[2] Advanced Materials Research Group, Faculty of Science & Technology, University Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.
[3] Renewable Energy Research Group, Faculty of Science & Technology, University Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

ABSTRACT

Solution approaches to zinc oxide (ZnO) nanorods is interesting because of their low growth temperatures and good potential for scale-up. Usually, the hydrothermal method involved two-steps which are seeding and dipping the conducting glass substrates in ZnO precursors. The size (diameter and length) of nanorods can be tuned by changing the dipping process parameters such as temperature, duration, precursor's concentration and pH. In this work, result showed that ZnO nanorods were successfully grow on Indium Tin Oxide (ITO) glass substrates with average diameter of 89 $\pm$ 1 nm and average length of 140 $\pm$ 1 nm that are going to be used in thin film solar cells.

Keywords: *ZnO nanorods, hydrothermal and solar cells*

1. INTRODUCTION

Zinc oxide (ZnO) is a II–VI semiconductor with a wide and direct band gap of about 3.37 eV (at 300 K) and a large free exciton binding energy of 60meV, high optical gain (300 cm^{-1}), high mechanical and thermal stabilities and radiation hardness. One-dimensional (1-D) ZnO nanomaterial recent studies are focused mostly on the correlation of nanoarchitecture morphology with deposition parameters and physical properties. However, achieving control over ZnO nanomaterial morphology is a challenging task [1]. One-dimensional (1D) nanostructures have been extensively studied because of their potential applications in nanoelectronic devices such as field-effect transistors, single-electron transistors, photodiodes, and chemical sensors. Therefore, 1D ZnO nanorods can be used for many applications, including ultraviolet light-emitting devices, field-effect transistors, solar cells, and chemical sensors. To grow ZnO nanorods, various synthesis methods have been utilized, such as vapor-liquid-solid (VLS) growth [2], metal organic vapor deposition (MOCVD) [3] and electrochemical deposition [4]. However, those methods require severe conditions or a catalyst for nanorod growth. The hydrothermal solution method has many merits that can make ZnO nanorods grow at low temperatures and at low cost. To fabricate ZnO nanorods in liquid solution, the effects of zinc salt, concentration of zinc salt, pH, growth temperature and growth time need to be investigated, because the morphology of the ZnO nanorods is affected by those process parameters. By growing highly oriented ZnO nanorods, the surface area per unit area can be increased, which will improve the performance of the nanodevices. The surface area of the nanorods is determined by the density and size of the nanorods. Therefore, the surface area of ZnO nanorods can be controlled by modifying the above-mentioned growing environments [5].

2. EXPERIMENTAL

a. Material Used

Zinc acetate dehydrate, $Zn(O_2CCH_3)_2$ (0.1M) was used as the zinc ion source, natrium hydroxide, NaOH (0.1M) as the reducing agent and methanol, CH_3OH as the solvent for the synthesis of ZnO nanoparticles. Zinc nitrate hydrate, $Zn(NO_3)_2.H_2O$ (0.014M) and methenamine, $(CH_2)_6N_4$ or HMT (0.014M) as the reactants in the chemical bath for ZnO nanorod growth.

b. ITO Glass Substrate Preparation

ITO glass substrates were immersed in distilled water that filled in 100 ml beaker and ultrasonic-cleaned for 5 min. After that the ITO glasses immersed in acetone and ultrasonic-cleaned for 5 min again. Finally the ITO glasses were rinsed with distilled water and dried in oven at 60°C for 10 min to remove residual water. After that the ITO glasses were kept in the drying cupboard in order to prevent the contamination to the ITO glass.

c. Synthesis of ZnO nanoparticles (np) and nanorods

The ZnO nanoparticles were sensitized by using 0.1M of natrium hydroxide and 0.1M of zinc acetate dehydrate as starting materials. 50 ml each of two solutions

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were mixed together and heated at 90°C for 1h in laboratory furnace. Finally whitish solution was produced and stable within two weeks. The ZnO nanoparticles were spin-casted on ITO glass substrate for five times with 500 to 2000 rpm between 10 to 20 s by using spin coater (Model WS-400B-6NPP/LITE) in seeding step. The coated glass substrates then dipped into the solution of 50 ml 0.014M zinc nitrate hydrate and 50ml 0.014M methanamine in sealed beaker for 1h with the temperature of heating was 90°C for growing the ZnO nanorods hydrothermally in laboratory furnace [6]. The steps of making the ZnO nanorods thin films can be understood more by looking the schematic illustration in Fig.1.

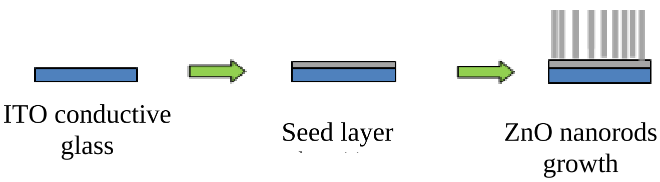

Fig 1: Schematic illustration of the fabrication process of ZnO thin film.

d. Characterization

The synthesized ZnO nanorods have been characterized with several equipments in aspect of its morphology and crystal structure. The instruments that have been used in characterizing the samples morphology was scanning electron microscope (SEM, Jeoul JSM-6360 LA) while X-ray diffraction (XRD, Rigaku Miniflex II, desktop) has been used in characterizing the crystal structures.

3. RESULTS AND DISCUSSION

a. ZnO Morphology

Fig. 2 shows the plane view and cross-sectional view of the nanorod arrays grown on ZnO seeded ITO glass substrates for 1h at 90°C via hydrothermal method. As a reminder, the ZnO seeding is a crucial step to ensure well orientation of ZnO nanorods growth on the ITO glass substrates [7-11]. By referring to Fig. 2, the ZnO nanorods covered almost entire area of ITO glass substrates even though its arrays were not too dense. In Fig. 2 (a), there were some very long rods existed, and this is due to the prior formation of rods in the precursor's solution before hydrothermal process and the rods have attached on the ITO glass substrate. However, these long rods were rare found on the ITO glass substrates during the observation through SEM. Most of ZnO nanorods in this work formed clusters (Fig.2 inset image). The clusters morphology shown in the image is common and it was suggested that multiple nanorods can be grown from a single aggregate of ZnO nano particles attached on the substrates [6].

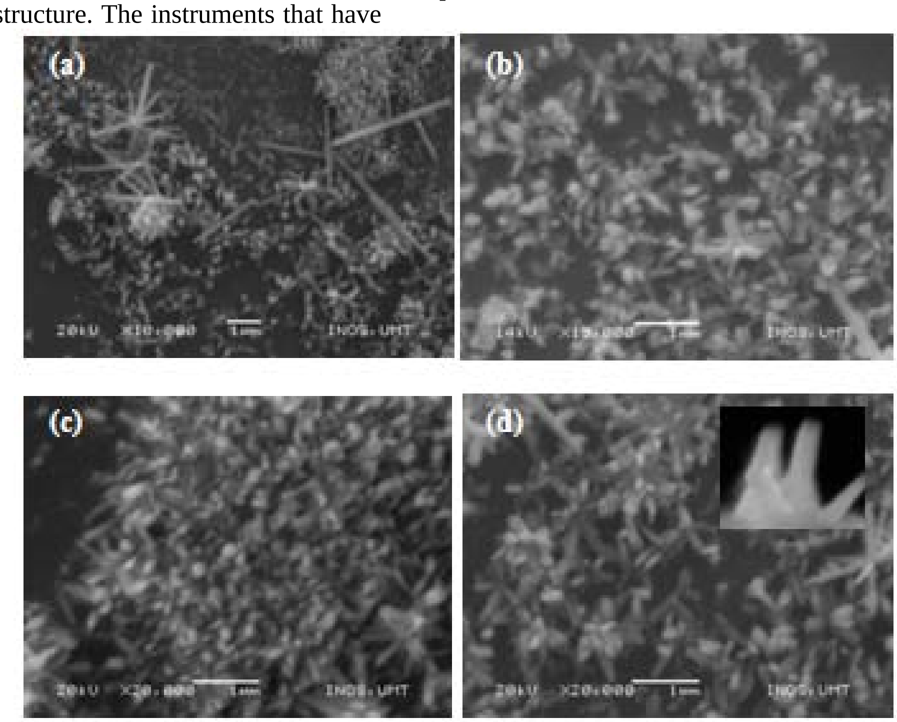

Fig. 2: (a), (b), (c) and (d) SEM images of ZnO nanorods at different spots grown on ITO glass substrates. The inset is corresponding cross-section close-up look of a ZnO nanorods cluster.

The glass substrates with ZnO seeds were annealed at 150°C for 15 min in furnace. The annealing step for glass substrates with ZnO seeds is essential to initiate chemical bonds between the seed layer and the substrate. The annealing process also helped to give the seed layer has good crystalline and also removed residual substances on the glass substrates which could be from water and reagent such as methanol [12]. Most of studies had proved that zinc oxide nanorod could grow into well-aligned nanoarrays in the presence of the seed layer otherwise, without the seed layer, zinc oxide nanorods grew randomly on the substrate. The intention of fabricating the seed layer is to significantly decrease the interface energy between zinc oxide crystal and the substrates in which can assist the growth of nanoarrays [10]. Fig. 3 illustrates the formation of ZnO nanorods through dehydration of $Zn(OH)_2$ and precipitated onto the substrates, leading to the formation of ZnO nanorods on the substrates.

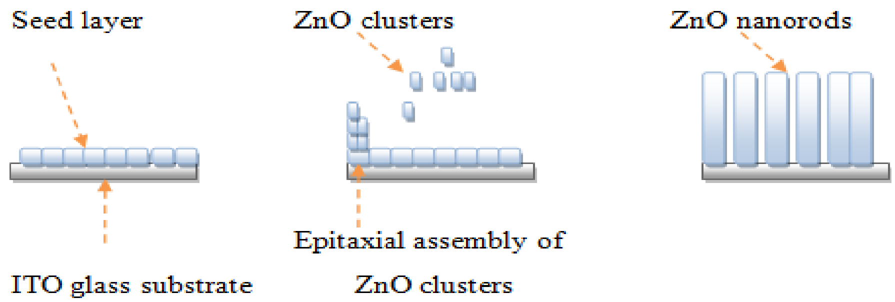

Fig.3: Schematic illustration of the possible growth mechanism for the formation of highly aligned c-axis-oriented ZnO nanorods grown on ZnO/glass substrates.

In 1h of hydrothermal process in this work, ZnO nanoclusters progressively precipitated on seed layer and build the ZnO nanorods on the substrates [9]. Even though the exact function of HMT during the growth is still unclear, it is believed to act as a weak base, which would slowly hydrolyze in the water solution and gradually produce OH^-. The detailed chemical reactions were:

$$C_6H_{12}N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \quad (1)$$

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

$$Zn^{2+} + 4NH_3 \leftrightarrow Zn(NH_3)_4^{2+} \quad (3)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \text{ or } Zn(NH_3)_4^{2+} + 2OH^- \rightarrow Zn(OH)_2(NH_3)_4 \quad (4)$$

$$Zn(OH)_2/Zn(OH)_2(NH_3)_4 \rightarrow ZnO + H_2O \quad (5)$$

The growth process of hydrothermally process can be controlled through the five chemical reactions listed above. All of the five reactions can be controlled by adjusting the growth time, temperature, pH value and etc. With the movement of the reaction equilibrium to the right side, ZnO will form through dehydration of Zn $(OH)_2$ and precipitate onto the glass substrates, leading to the formation of ZnO nanorods on the ITO glass substrates [13]. In this work, ZnO nanorods were successfully growth with average diameter of 89 $\pm$ 1 nm and average length of 140 $\pm$ 1 nm.

b. X-ray diffraction characterization

Referring to XRD relative peaks intensities of ZnO in fig 4 are distinct from those of ZnO powders. The (002) peak is very strong compared with other peaks which are (100) and (101). The results signify that ZnO nanorod arrays are highly aligned perpendicular to ITO glass substrates with the c-axial growth direction. The degree of orientation can be demonstrated by the relative texture coefficient [14], given by

$$TC_{002} = \frac{I_{002}/I^o_{002}}{I_{002}/I^o_{002} + I_{101}/I^o_{101}} \quad (6)$$

Where TC_{002} is the relative texture coefficient of diffraction peaks (0 0 2) over (1 0 1), I_{002} and I_{101} are the measured diffraction intensities due to (0 0 2) and (1 0 1) planes, respectively while I_{002}^0 and $I_{101}^0$are the correlating values of standard PDF (File No. 01-089-0510) measured from randomly oriented powder samples. For materials like powder that has random crystallographic orientations, the texture coefficient was 0.5 [15]. The value of synthesized nanorod arrays was 0.94, which proves an extremely high c-axis orientation of the crystals. The XRD result hints that prepared nanorod arrays are highly crystalline having wurtzite structure favored c-axis orientation. No secondary phase was detected within the limit of XRD measurement.

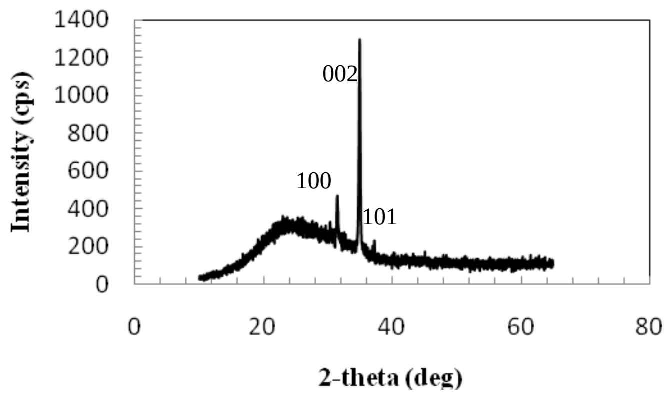

Fig 4: XRD pattern of the as-prepared ZnO nanorods.

As theory claims, the ZnO {0001} faces are the highest-energy low index planes and that will be a problem in explaining the dominance of c-axis texturing in ZnO islands, nanorods and thin films. The elevated temperatures deposited ZnO thin films are commonly oriented perpendicular to the substrate surface in c-axis, even on substrates that have amorphous structure such as glass. Furthermore, most of single-crystalline ZnO nanorods synthesized without the use of epitaxy also grow along the c direction, regardless of growth method such as gas or solution phase. From these growth habits, it can be suggested that the c-axis is the fastest growth direction and therefore that ZnO {0001} is the low-index surfaces with the highest energy, in agreement with theory. The expectation of ZnO film/rods orientation is determined by the nucleation and growth of the first few layers of zinc and oxygen atoms is reasonable because the alignment of seeds occur on disparate, nonepotaxial surfaces. The interactions of ZnO substrates are probably not an important driving texturing in ZnO seeds nucleation disregard the high energy of the {0001} surfaces [16].

4. CONCLUSIONS

In summary, aligned ZnO nanorod samples have been grown on ITO glass substrates through 1h and 90°C growth route hydrothermally. Samples obtained from this project had the XRD peaks of (100), (002) and (101). The most dominant peak of ZnO nanorods in this work were (002) with relative texture coefficient of 0.94. This approved that the nanorods have grew perpendicularly to substrates. From the morphology study we obtained averagely 89 $\pm$ 1 nm in diameter and 140 $\pm$ 1 nm in length of Nanorods that are going to be used in thin film solar cells.

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