Growth of ZnO Nanorods Synthesized via Chemical Bath Deposition at Different Reaction Times and Precursor Concentrations

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Abstract. The characteristics of ZnO grown via chemical bath deposition on an FTO glass substrate at different reaction time and precursors concentration have been examined. The ZnO seed was firstly spin coated at 500 rpm for 5 seconds onto an FTO glass substrate and then at 3000 rpm for another 30 seconds. The coated substrate was heated at 130 °C to remove the solvent. The growth of ZnO nanorods was performed via chemical bath deposition (CBD) at various precursor concentrations and reaction times. The morphology of the obtained ZnO nanorods were characterized using a field-emission electron microscope (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDX) to reveal the morphology and elemental composition of the nanorods, whereas X-ray diffraction (XRD) was used to examine the crystal structure. The results showed that the ZnO products have nanorod structure and sizes for each concentration. The results of this morphology were supported by the results from XRD. XRD patterns revealed that the formation of nanostructure of ZnO has been obtained at the reaction time of 2 hours, however, the optimum formation time was proven to be at 3 hours. The results also revealed that ZnO nanorods with a precursor concentration of 0.0375 M has the optimum formation of ZnO nanorod in terms of size and distribution of the nanorods.

Keywords: Chemical Bath Deposition, Nanorods, Zinc Oxide

1. Introduction

Zinc Oxide (ZnO) is one of important semiconductors and has been one of well-researched, especially in the forms of nanomaterials, because of its unique properties and advantages. Its unique properties include direct wide band gap of 3.37 eV, large exciton binding energy of 60 meV, and low cost of production [1-5]. This material has also been used for many applications in various fields such as gas sensor [6], dye-sensitized [7], perovskite solar cells [8], light-emitting diodes [9], photocatalyst [10], and piezoelectric device [11]. Many varieties of ZnO nanostructures such as nanorods [12], nanotube [13], snow-flake [11], nanobelts [14], nanosheets [15], nanowires [16], nanospheres [17], lotus like [18], brush-pen-like and flower-like [11] have been reported by many investigators.
ZnO can be synthesized via several methods such as hydrothermal process [19], thermal evaporation process [11], solvothermal [20], sol-gel [17], solid state reaction [18], electrodeposition and wet chemical method [21]. Electrodeposition, hydrothermal process, and chemical bath deposition (CBD) are chemical based methods that can be used for one dimensional ZnO nanostructure. In terms of growth process, CBD is one of the simple methods because it can be grown at low temperature and cheap equipment. The chemical bath deposition involves 2 step processes, i.e. nucleation on a substrate followed by the growth to form a solid phase from a solution [22]. During the formation, however, the parameters of this two-step process such as precursor concentrations and time [23], seeding layer [24], and temperature [25] may affect the structure and morphology of ZnO nanorods and thus its properties. Despite its wide use and important application, there are not many references discusses the effect of different reaction times and precursors concentration on the growth of ZnO nanorods. The present work aiming at evaluating the effect of different reaction times and precursor concentrations on the characteristics of ZnO nanorods synthesized and grown on a glass substrate via chemical bath deposition method. The results of the grown ZnO nanorods could be applied as a semiconductor in the renewable energy devices such as dye-sensitized and or perovskite solar cells.

2. Experimental method
2.1. ZnO Seeding
The seed was synthesized through a sol-gel process using precursors of NaOH 0.03 M and zinc acetate dihydrate (Zn(CH₃COOH)₂·2H₂O) 0.02 M solved in methanol under magnetic stirring at 60 °C for 2 hours. The ZnO seed in the forms of solution was cooled to room temperature and was firstly spin-coated at 500 rpm for 5 seconds onto an FTO glass substrate followed at 3000 rpm for another 30 seconds until the ZnO seeds spread equally on the FTO surface. The coated substrate was heated at 130 °C to remove the remaining solvent. Thin white layer of precipitates was observed on the surface of the FTO glass.

2.2. Growth ZnO Nanorods
The growth of ZnO nanoparticles was performed via chemical bath deposition at various precursor concentrations and reaction times. For the precursor concentration, the ZnO seed was soaked in the precursors with a position ZnO seed layer facing the bottom of the beaker glass containing hexamethylenetetramine (HMTA) solution and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) in water with concentration variations of 0.025, 0.0375, 0.05, and 0.075 M at 130 °C for 3 hours. For the variation in reaction times, the precursor concentration was fixed at 0.025 M with different reaction times of 2, 4, and 6 hours. After CBD reaction was completed, the glass substrate was washed using deionized water and was heated at 130 °C for 5 minutes before being ready for the characterization.

2.3. Characterization
The characteristics of the ZnO nanorods were investigated through surface morphology and crystal structure. The morphology of ZnO nanorods was investigated using a field-emission electron microscope (FE-SEM, FEI Inspect F50) to reveal the morphology of the nanorods, whereas X-ray diffraction (XRD, PANalytical X’Pert PRO) operated at 40 kV and 30 mA with Cu Kα radiation (λ = 1.5406 Å) was used to examine the crystal structure.

3. Results and Discussion
3.1. Structure and Surface Morphology
3.1.1. Effect of precursors concentration on ZnO nanostructure. In this study we set deposition time at its optimum value of 3 hours and the precursor concentration variations of 0.025 M, 0.375 M, 0.05 M, and 0.075 M at 130 °C. Figure 1(a) shows secondary electron image of the obtained ZnO nanorods with 0.025 M precursor concentration. As can be seen from the figure, the ZnO nanorods have the
smallest diameter compared to the others, but with random ZnO nanorod orientation. Figure 1(b) shows secondary electron image of the obtained ZnO nanorods with 0.035 M precursors concentration. The image reveals that the nanorod diameter is larger with the direction of nanorod is more upright and straighter than that of the nanorods from the 0.025 M. Figure 1(c) shows secondary electron image of the obtained ZnO nanorods with 0.05 M precursors concentration. The ZnO nanorods have larger diameters as compared to the previous two lower precursor concentrations. As can be seen from the figure, the ZnO nanorods structure are arranged tightly with each other and show a distinct hexagonal structure. Figure 1(d) shows secondary electron image of 0.075 M precursors concentration. As can be seen, ZnO nanorods show the largest diameter compared to the others with hexagonal structure but almost clump together. It is expected that this is because at 0.075 M concentration, the precursor has been saturated in the solution. The average diameters of the obtained nanorods at these different concentrations are 68 nm, 86 nm, 235 nm, and 375 nm for 0.025 M, 0.035 M, 0.05 M, and 0.075 M, respectively. These results are in agreement with the results found by others [12, 26].

Figure 1. Secondary electron images of ZnO nanorods synthesized with different precursor concentrations: (a) 0.025 M, (b) 0.0375 M, (c) 0.05 M, and (d) 0.075 M.

3.1.2. Effect of reaction time. Figure 2 shows all secondary electron images of the microstructure ZnO nanorods synthesized at 130 °C with precursors concentration of 0.025 M but different reaction
times. Figure 2(a) shows the secondary electron images of ZnO nanorods synthesized for 2 hours. The image reveals an early establishment of the nanorods growth formation with random direction and small nanorod diameters. Figure 2(b) shows ZnO nanorods morphology with reaction time of 4 hours. The product is showing a denser morphology with larger diameter with more upright and straight direction compared to the previous reaction time of 2 hours. Figure 2(c) is ZnO nanorods morphology with the reaction time of 6 hours. Interestingly, as can be seen in the figure, the morphology of the ZnO nanorods seem to grow with a tendency to form flower-like nanorod structure. This tendency could be as a result of the prolonged reaction time in which instead of growing in an upright position, it tends to form branches resulting in a flower-like morphology.

Figure 2. SEM images of ZnO Nanorod Synthesized with different time reaction. (a) 2 hours. (b) 4 hours. (c) 6 hours.

3.2. Phase Structure Analysis

3.2.1. Influence of precursor concentration. In this study, to examine the effect of precursor concentration on the phase formed, the deposition time was fixed for 3 hours at different precursor concentrations. The X-ray diffraction patterns are given in Figure 3.

Figure 3. X-ray diffraction patterns of ZnO nanorods synthesized with different precursor concentrations. (a) Pure ZnO, (b) 0.025 M, (c) 0.05 M, and (d) 0.075 M.
As can be seen in Figure 3, most of the diffraction patterns can be indexed to the ZnO nanorods with the planes (100) (002) (101) (102) (110) (103) (200) (112). Some other diffraction patterns of impurities peaks, however, are also still detected. It seems that during the synthesis, not all of the precursors form the end product. This result is in accordance with what have been found by other investigators on the diffraction patterns of ZnO nanorods [20].

The strong intensity peak indicates that ZnO nanorods product have good crystallinity. In this result, however, there is a tendency that at precursor concentrations of 0.05 M and 0.075 M, the crystal grows to form (002) preferred orientation. It is expected that the growing of the crystal at these precursor concentrations is at the plane (002) as other investigators have been also found [16]. The results from the X-ray diffraction patterns reveal that the ZnO nanorods layer on the glass substrate have been formed characterized by three dominant peaks corresponding to (100), (002), and (101) orientations. The (002) reflection peak has very strong intensity in all precursor concentration, with the highest intensity is the one from 0.075 M, followed by 0.05 M and 0.025 M.

3.2.2. Influence of reaction time. X-ray diffraction patterns of the different reaction time at a fix precursor concentration are shown in Figure 4. As can be seen in the figure, most diffraction peaks can be indexed to the phase of pure ZnO similar to that of different precursors concentration with several peaks from the impurities. The diffraction patterns show that the peaks intensity from the obtained ZnO nanorods at 2 and 4 hours of reaction time are still are still low as an indication of low crystallinity due to the formation of amorphous phase and or nanosized materials. On the contrary, at 6 hours of reaction time, the intensity increases. This can be understood since the longer the reaction time the more the time for self-arrangement of the atoms to form a crystalline phase.

![Figure 4. X-ray diffraction patterns of ZnO nanorod synthesized with different reaction times (a) Pure ZnO, (b) 2 hours, (c) 4 hours, and (d) 6 hours.](image)

4. Conclusion
A simple synthesis of ZnO nanorods on a glass substrate via chemical bath deposition with different precursor concentrations and reaction times has been successfully performed. In this work, precursor concentration and reaction time both play crucial roles in determining the morphology and structure of the obtained ZnO nanorods as revealed by the results from secondary electron images and X-ray diffraction patterns. It has also been shown that ZnO nanorods with a precursor concentration of 0.0375 M has the optimum formation of ZnO nanorod in terms of size and distribution of the nanorods.
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