

HYDROTHERMAL SYNTHESIS OF ROD AND CHRYSANTHEMUM LIKE NANOSTRUCTURED ZnO

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ABSTRACT

Rod and chrysanthemum-like nanostructured ZnO thin film have been prepared hydrothermally in NaOH and NH₃ solution utilizing zinc nitrate hexahydrate as the precursor. ZnO thin films were grown on ITO glass substrate with the seed layer of zinc oxide. Perpendicularly aligned arrays of corrugated ZnO nanorods were grown in NaOH solution, while the chrysanthemum like structure was obtained in ammonia solution. X-Ray diffraction patterns confirmed that both morphologies presenting wurtzite crystal of ZnO. The nanorod showed strong (002) orientation of ZnO.

Keywords: Semiconductor, ZnO, Hydrothermal, Nanostructures

INTRODUCTION

Semiconductor thin films with dimension in the nanometer scale were still in a research stages. The research has been increased significantly because of their scientific importance likes electrical, optical and chemical properties of the resulted semiconductor materials that can be transformed by changing their particle size [1]. Since carbon nanotubes were discovered by Iijima [2], nanostructure semiconductor material like ZnO has been successfully synthesized to many shape and structure by various routes. ZnO is one of semiconductor material which has many functions in optoelectronics application. ZnO has the wide bandgap (3.37 eV) with large binding exciton energy (60 eV) at room temperature. Various chemical synthetic methods such as hydrothermal, sol gel, precipitation, electrochemical deposition, microwave assisted, and aqueous solution method at low temperature have been developed to prepare ZnO nanoparticles like nanorods [3-4,7], nanobelts [5], nanoflowers [4-5], nanodiscs [4], nanoribbons [8], nanocombs [8], nanotubes [9], and nanowires [4].

Generally, the particle properties such as morphology and size can be controlled via hydrothermal process by adjusting the reaction temperature, time, and concentration of precursors. Hydrothermal synthesis of ZnO powders has four advantages; powders with nanometer-size can be obtained, the reaction condition was moderate, powders with different morphologies can

be obtained by adjusting the reaction conditions, and the as-prepared powders have different properties from that of the bulk [5].

Most hydrothermal synthesis of ZnO nanorods relies on the use of methenamine (C₆H₁₂N₄) as capping agent and metal zinc precursor [1]. Weak base as an effective capping agent in ZnO nanorod synthesis, template free in the process of ZnO nanorod synthesis, and easy to get were to be the several advantages of methenamine [1]. But the usage of methenamine made the cost of ZnO nanorod synthesis increases significantly. Although non toxic to aquatic organisms, it is dangerous to the environment. In this paper, we tried to replace methenamine with NaOH and NH₃ as a base in ZnO nanorod synthesis. Consequently, NaOH and NH₃ could be used as a good mineralizer due to its alkalinity. As the illustration, Yu et al. [6] confirmed that Li et al. have studied well aligned ZnO nanorods with diameters of 200–400 nm, which were synthesized via an aqueous solution route in a constant equimolar aqueous solution of ZnNO₃·xH₂O and C₆H₁₂N₄ at 95 °C for 10 h, and demonstrated that well-aligned ZnO nanorods could be grown on various substrates coated with ZnO film and Youngjo et al. reported on ZnO nanorod arrays grown on silicon substrates with zinc metal layer in ammonia aqueous solutions. These researchers illustrate that the aqueous solution approach toward ZnO nanorod array is a low temperature and simple process. So in this research we tried to develop hydrothermally ZnO synthesis route

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utilizing zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with ammonia (NH_3) and sodium hydroxide (NaOH) as its capping agent in modified ITO substrate by ZnO seed layer from Zinc Acetate Hexahydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$) in ethanol system. As we know, NH_3 and NaOH are lower cost and easier to get than methenamine. ZnO nanorod films will be prepared as Lee et al. [11] that fabricate ZnO nanorod as a template to prepare vertically-aligned TiO_2 nanotubes by etching and deposition process in liquid phase deposition (LPD) [10]. Although we tried with the same method as Lee et al. [11], we got different results that will be discussed in this paper. It will be shown that different treatment and condition may result different shapes nanostructured ZnO. We got reproducible and uniform rod and chrysanthemum like ZnO nanostructures in our method.

EXPERIMENTAL SECTION

Materials

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zinc acetate hexahydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$), ammonia (NH_3), and sodium hydroxide (NaOH) were from Merck. Tin-doped indium oxide (ITO) glasses were used as film substrates in this study.

Instrumentation

X-Ray Diffraction (XRD, Shimadzu XRD-6000 Elmer) and Scanning Electron Microscope (SEM, JEOL JSM-6360 LA) were used to analyze crystal phase and morphology of ZnO films, respectively.

Procedure

Firstly, ZnO seed layer was prepared by dissolving of 0.47 g $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of ethanol at room temperature. Pre-cleaned ITO glass (2x1 cm) was immersed in the resultant solution. The system was packed in Teflon bottle. ZnO seed layer will stick on ITO glass substrate after heating process in Teflon line bottle at 130 °C for 2 h. Then, modified ITO glass substrate was dried in the air for a while.

ZnO rod- and chrysanthemum like structure were prepared by dipping of modified ITO glass substrate in aqueous solution of 0.8 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.8 M NH_3 , and in aqueous solution of 0.04 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.4 M NaOH , respectively. The methods were modified from Yu's and Yoshikawa's methods [7,10]. ZnO will grow as chrysanthemum like structure by heating the first mixture at 90 °C for 4 h. While, rod-like ZnO structure was obtained by heating the second mixture at 110 °C for 20 min. After heating process, each

film was washed by double distilled water into neutral pH condition to remove any residual salt or hydroxide complex and then dried in air. The films were characterized using XRD and the morphology of films was investigated by SEM.

RESULT AND DISCUSSION

ZnO seed layer as the layer of modified ITO glass substrate was prepared by heating of ITO glass substrate in ethanolic solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 6\text{H}_2\text{O}$. The existence of ZnO seed layer decreased interfacial energy between crystal cores and substrate, so facilitated the nucleation process.

From Fig. 1, it is shown that the highest diffraction peak of ZnO seed layer at 36° corresponds to (101) diffraction peak with interplanar distance of 0.2473 nm. Peak at 34° corresponds to (100) diffraction peak ($d=0.2805$ nm), and the one at 32° corresponds to (002) diffraction pattern ($d=0.2603$ nm). The crystal type of ZnO seed layer was identified as wurtzite.

Jung et al. [12] reports that hydrothermal synthesis of ZnO may result in various morphologies such as rod, flower, disk, cup, and sphere like structure. It was also shown that the XRD patterns of the resulted ZnO have strong relationship with the resulted morphologies. ZnO in one dimensional structure like rod shape has diffraction pattern with (002) diffraction peak as the highest peak. While the three dimensional morphology has a specific order and ratio of peaks intensity of wurtzite crystal, i.e (100), (101), and (002) diffraction peaks. Flower, cup, or sphere morphologies have diffraction patterns with sequence intensity of $d_{[101]} > d_{[100]} > d_{[002]}$ [10]. While disk morphology has diffraction pattern with intensity sequence of $d_{[101]} > d_{[100]} = d_{[002]}$. Therefore, we assume that ZnO seed layer which has diffraction pattern as in Fig. 1 will exist in flower, cup, or sphere shape as evidenced by their diffraction peaks sequence of $d_{[101]} > d_{[100]} > d_{[002]}$. The existence of flower, cup, or sphere morphology may cause the crystal grow in 3D as directed by the crystal axis. Thus, reducing the intensity of $d_{[002]}$ as the signature of rod-like ZnO [12].

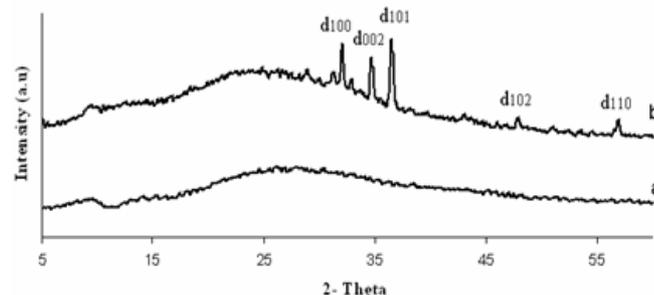


Fig 1. Diffraction patterns of (a) glass substrate and (b) ZnO seed layer on glass substrate

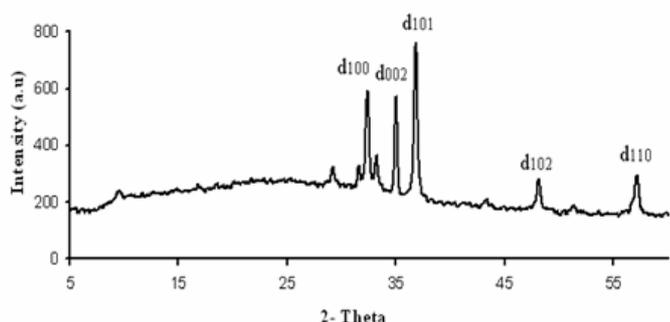


Fig 2. Diffraction pattern of chrysanthemum like ZnO

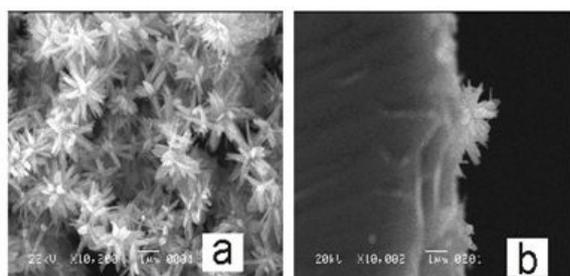


Fig 3. SEM images of ZnO thin film from NH_3 : (a) top view; (b) cross sectional view

After ZnO seed layer has been successfully formed on ITO substrate, the modified substrate was then applied as a substrate in preparation of ZnO thin film nanostructure utilizing $\text{Zn}(\text{NO}_3)_2$ and NH_3 with molar ratio of 1:10. The XRD pattern and SEM images of the resulted nanostructured ZnO were shown in Fig. 2 and Fig. 3, respectively.

From Fig. 2, it is clear that the sequence of diffraction peaks is $d_{[101]} > d_{[100]} > d_{[002]}$. ZnO thin film obtained hydrothermally from $\text{Zn}(\text{NO}_3)_2$ with NH_3 as the alkaline solvent did not exist in single rod shape, but as a bunch of flower-like structure. Each bunch has one central point in the centre. It is predicted that the rod started to grow from the centre to all directions composing chrysanthemum like structure. The size of a bunch of chrysanthemum was up to $1 \mu\text{m}$. It was acquired from the approximately as estimated from the SEM image (Fig. 3). Such morphology was often called chrysanthemum like structure [13].

We also used the modified ITO glass as film substrate in the preparation of nanostructured ZnO using the same zinc nitrate precursor with NaOH as the alkaline solvent. By this route, we got white solid which was strongly adhered on the surface of the ITO glass substrate. The film formed was thinner than that of ZnO chrysanthemum like. Fig. 4 showed the diffraction pattern of the white thin layer. It is clear that (002) diffraction pattern was the highest peak indicating the presence of highly oriented ZnO in its c-axis. The growth of rod was along the c-axis. The morphology of ZnO thin

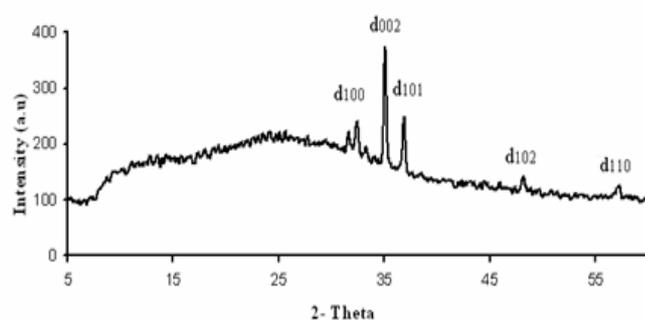


Fig 4. XRD patterns of rod like structure ZnO

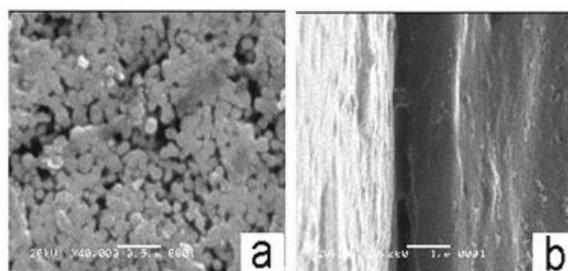


Fig 5. SEM images of ZnO thin film from NaOH: (a) top view; (b) cross sectional view

film from NaOH solution was then evaluated by SEM as shown in Fig. 5.

The top view image displayed rounded base of rods which are aligned vertically on the ITO glass substrate. Unfortunately, the cross section view did not clearly show the rows of the vertical rods. It may be due to fine morphology of the nanorods. The rod diameter is about 125 nm as calculated from the SEM image. The rod length reached $0.75 \mu\text{m}$. This dimension is smaller than that reported by Jung et al. [4], which was 180 nm in the diameter and $1.5 \mu\text{m}$ length. Hydrothermal treatment in NaOH solution was effectively suppress the growth of multiple rods as occurred in NH_3 alkaline solution resulted vertically oriented rod like nanostructured ZnO.

CONCLUSION

In summary, we have shown that different alkaline solution as hydroxide anion generating agent generated different ZnO nanostructures after hydrothermal treatment. Rod like ZnO nanostructure was obtained by using NaOH as hydroxide anion generating agent, while chrysanthemum like was obtained by using NH_3 . Short hydrothermal treatment under NaOH solution at $110 \text{ }^\circ\text{C}$ has shown to hold the flower like nanostructure growth of ZnO.

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