HYDROTHERMAL GROWTH OF ZNO NANOWIRES

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Abstract. The hydrothermal method provides a wide range of possibilities for processing of materials whether it is bulk single crystals, or fine particles, or nanowires. Hydrothermal materials processing has a lot of advantages such as a singles step process, low energy technique and low temperatures. In this paper present the results of synthesis of ZnO nanowires by hydrothermal method from 0.04 M of Zn(NO₃)₂, 6H₂O and C₆H₁₂N₄ solutions using ZnO:Al thin film substrate. Temperature was keep constant at 90°C for 2 hours. Nanowires of ZnO were clean with DI water and drayed with nitrogen and structural and morphological characterized.

Keywords: synthesis, hydrothermal, ZnO, nanowires

1. INTRODUCTION

One-dimensional nanostructures exhibit interesting electronic and optical properties for electronic and solar cells applications. ZnO nanowires present o big interest in the last year because is a non toxic, low cost material and good properties for a wide range of applications. Zinc Oxide is a promising material of photonics because of its wide bandgap of 3.37 eV and high exciton binding energy of 60 meV. The wide bandgap makes ZnO a suitable material for short wavelength photonic applications while the high exciton binding energy allows efficient exciton recombination at room temperature. It is used as varistors, transparent high power electronics, optical waveguides, piezoelectric converters, gas-sensing analyzers, window materials for display and solar cells, etc. In the recent years, ZnO bulk crystals are used as the substrate materials for the epitaxial growth of GaN[1]. Many researcher groups reported results about ZnO nanoparticles [2-8]. Hydrothermal synthesis is generally defined as crystal synthesis or crystal growth under high temperature and high pressure water conditions from substances which are insoluble in ordinary temperature and pressure (<100 °C, <1 atm). The solvent properties for many compounds, such as dielectric constant and solubility, change dramatically under supercritical conditions [9]. The formation mechanism of metal oxide particles from metal nitrate solution is as follows:

First, hydrated metal ions are hydrolyzed to metal hydroxide. Then, metal hydroxides proceed to precipitate as metal oxides through dehydration [10, 11].

\[ M(NO_3)_2 + xH_2O \rightarrow M(OH)x + xHNO_3 \]
\[ M(OH)x \rightarrow MO_{x+y} + x/2 H_2O \]

Hydrothermal synthesis in supercritical water has advantages for synthesis of multi metal oxide compounds because the reaction rate is enhanced more than 10³ times that under the conventional hydrothermal conditions owing to the low dielectric constant (<10) as well as products with high crystallinity [12-14]. The particle size of metal oxide depends on the hydrolysis rate and solubility of the metal oxide. To achieve the control of the solvent field during nucleation and crystallization of particles, hydrothermal conditions of temperature and pressure can be varied in subcritical and supercritical water. Hydrothermal methods for preparing fine metal oxide particles in subcritical and supercritical water have been developed using batch reaction [15-27, 40-50] and flow reaction systems [28-39].

Synthesis of ZnO nano- or micro-structures from Zn(NO₃)₂-HMT system has been reported in recent years [51-52]. It is generally considered as a very simple and novel process. The understanding of the growth mechanism of varieties of morphologies of ZnO still needs further improvement. On the basis of other researchers’ previous analysis [53] the growth process of ZnO crystallites is generally accepted via the following mechanism:

\[ (CH_2)_2N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \]
\[ NH_3 + H_2O \rightarrow NH_4^+ + OH^- \]
\[ Zn^{2+} + NH_3 \rightarrow Zn(NH_3)_4^{2+} \]
\[ Zn(NH_3)_4^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} + 4NH_3 \]
\[ Zn^{2+} + 4OH^- \rightarrow Zn(OH)_4^{2-} \]
\[ Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2OH^- \]

In the diluted ammonia aqueous solution, Zn(NH₃)₄²⁺ and Zn(OH)₄⁻ can coexist. Therefore Zn(OH)₂⁻ is more stable and can be formed from the transformation of Zn(NH₃)₄²⁺ (Eq. (4)). In dilute ammonia solution, the amount of OH⁻ is few (the pH value is about 10) and the formation of ZnO nuclei largely follows the reaction steps (1) → (2) → (3) → (4) → (6). In this case, the forming of ZnO nuclei is slow and it becomes the controlling step for synthesis of the ZnO films [54].

2. EXPERIMENTAL

Aluminum-doped zinc oxide films were deposited on glass substrates by using an rf magnetron sputtering method. The glass substrates were cleaned by using ultrasonically bath and follow 3 steps: first with acetone, second with methanol, and the last with demonized (D.I) water, and then dried by blowing nitrogen over them. The RF (radio frequency) magnetron sputtering system
that we used in our study had a turbo-pumped, deposition chamber and three targets to enable simultaneous sputtering. The target used for study, it is a ceramic 2 inch disk type ZnO doped with Al2O3 (2 wt.

<table>
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<tr>
<th>Table 1. Deposition conditions of AZO thin films</th>
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<tr>
<td>Target</td>
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<td>Substrate</td>
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<td>Substrate temperature</td>
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<td>Power</td>
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<td>Distance between target and substrate</td>
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The surface morphology and structure of the films were examined by employing a scanning electron microscope (SEM, Zeiss Auriga) and X-ray diffraction (X Bruker-AXS type D8 Advance).

Synthesis of ZnO nanowires on Al:ZnO (AZO) substrates, was carried out by hydrothermal process at 90 °C using zinc nitrate hexahydrate (Zn(NO3)2 6H2O and hexamethylenetetramine C6H12N4 (HMT) as source materials. For synthesis, 20 mmol Zn(NO3)2 6H2O was dissolved in 25 mL of DI water and 20 mmol C6H12N4 was dissolved in 25 mL of DI water, then all the above solution was mixed, and togeder with samples of AZO thin fims was heated at 90 °C for 2 h in an electric oven. Finally, the samples with ZnO nanowires was washed thoroughly with deionized water, dried with nitrogen and placed in a container at 25 °C for 24 h.

The surface morphology and structure of the ZnO nanowires were examined by employing a scanning electron microscope (SEM, Zeiss Auriga) and X-ray diffraction (XRD, PANalytical's X'Pert PRO MRD).

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of Al-doped ZnO film. Film show a diffraction peak at 20 near 34°, indicating typical hexagonal wurtzite structure with (002) preferred orientation. It indicates that Al doped ZnO film maintain the hexagonal wurtzite structures [55].

SEM micrographs of AZO films are shown in Fig. 2. It can be seen from Fig. 2 that the surface is almost uniformly covered with grains in average by the same dimensions.

Synthesis of ZnO nanowires on Al:ZnO (AZO) substrates, was carried out by hydrothermal method. Structural characterization was performed by X-ray diffraction using diffractometer X Bruker-AXS type D8 Advance with X-ray tube anode Cu, Ni filter ks, goniometrul vertical. Step 2 theta was 0.04°, scanning speed of the recording 2s/step and recording domain between 20-80°. Recorded spectrum is shown in Figure 1. Identification of zinc oxide was performed using the database International Center for Difraction date. X-ray diffraction (XRD) examination of the samples resulted patterns as shown in figure 1, indicating that the nanowires is highly crystallized. Figure 1 shows the XRD pattern of the ZnO nanowire growth on a Al:ZnO thin film substrate by using the hydrothermal synthesis process. A dominant diffraction peak for (002) indicates a high degree of orientation with the c-axis vertical to the substrate surface.
The general morphology of ZnO nanowires was obtained using field emission scanning electron microscopy. As shown in Fig. 2, ZnO nanowires were vertically well aligned with uniform length, diameter and distribution density. The average diameter and length of the ZnO nanowires grown for 50 nm and 170 nm, respectively. The SEM observations along with XRD results suggest that the well-aligned ZnO nanowires are of good crystal orientation and morphology.

4. CONCLUSIONS

ZnO nanowires has been prepared from a mix of zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O and hexamethylenetetramine C$_6$H$_{12}$N$_4$ (HMT) on Al doped ZnO thin film. Temperature of hydrothermal process was kept at 90°C for 2 hours. ZnO nanowires were placed in a container at 25 °C for 24 h.

XRD pattern of the ZnO nanowire growth on a Al:ZnO thin film substrate. A dominant diffraction peak for (002) indicates a high degree of orientation with the c-axis vertical to the substrate surface.

SEM images show that a dense array of hexagonal ZnO nanowires having a diameter of from 25nm to 90 nm and length between 100 and 170nm.

5. REFERENCES


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