Research Paper

Growth of Sheet-like ZnO Nanostructures on ZnO nano rods using Chemical Bath Deposition

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Abstract We demonstrate the growth of a sheet-like ZnO membrane on ZnO nano rod layers. The growth process is composed of 3 steps of ZnO seed formation, ZnO nano rod growth and sheet-like ZnO membrane formation on those nano rods. To confirm the fundamental growth mechanism, the lattice structures of each step were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM) measurement. Analysis of the relation between the texture coefficient and the surface shape of the ZnO membrane on the ZnO nano rods shows that the surface morphology of ZnO nano structures can be controlled using the temperature of the growing solution and the concentration of the chemical solution.

Keywords: Zinc oxide, Nano rods, Nano sheet, Chemical bath deposition, Nanostructure, Surface morphology

I. Introduction

Recently, due to the good functional properties of nanomaterial compared to those of bulk material, various synthesis methods of nanostructures have been proposed. Especially, ZnO nanostructures have been widely studied because of their interesting functionalities,

including electrical [1], optical [2–4], and piezo-electric characteristics [5]. With proper choices of materials and conditions of synthesis, ZnO can be synthesized in many different nanostructure forms, including nano rods, nanowires, nano walls, nanotubes, etc [6,7]. ZnO nano structures are used in the field of gas sensors⁸ and solar energy [9]; these materials have large surface to volume ratio, which enhances sensor response. ZnO nano structures can be synthesized by many growing techniques, such as molecular beam epitaxy (MBE) [10], radio frequency (RF) sputtering [11], pulsed laser deposition (PLD) [12] and atomic layer deposition (ALD) [13,14], chemical vapor deposition (CVD) [15], etc. However, the control of the growth methods requires high vacuum and high temperatures. To avoid a high cost of fabrication, chemical bath deposition (CBD) [7] is used because it enables large areas of nanostructured surface to be easily grown on the substrate and controlled by concentration of the compounds, temperature, and growth time. In addition, spin-coating methods allow the formation of ZnO seeds on wide areas of the substrate. The characteristics of the film

can be controlled by varying the growth conditions, such as the speed of rotation, the number of coatings, and the concentrations of the precursors.

In this paper, we demonstrate the growth of ZnO nano sheets using chemical bath deposition with varying of the growing conditions such as the temperature and concentration of the solution. The results show that the maximum surface/volume ratio can be achieved with a 160°C growth temperature. Also, we demonstrate the tendencies of the surface energy of the polar and non-polar surfaces, which can be inferred from the texture coefficients.

II. Experiments

1. ZnO Seeds

To prepare for the growth of the ZnO nano rods, we used spin coating to deposit ZnO seeds on a silicon substrate. Zinc acetate dehydrate (1 mmol) and lithium hydroxide monohydrate (1.4 mmol) in ethanol (50 ml) were spin coated (e-flex, SC40P) on the Si surface for 20 seconds at 3,000 rpm. After the spin coating, the Si substrate was heated to 350°C for 10 minutes on a hot plate (Corning, PC-420D). The processes of spin coating and curing were repeated 10 times. Finally, the spin coated ZnO seeds were annealed for 1 hour at 500°C under nitrogen gas condition in a furnace (Pluskolab, CRF-ST).

2. ZnO Nano rods

The aqueous solution is composed of a chemical mixture with 0.1M zinc nitrate hydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.1 M hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, HMT) in DI water;

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Figure 1. Schematics of ZnO wire/film growth.

solution is stirred at 300 rpm and 90°C for 24 hours. Afterwards, to develop ZnO nano rods, Si substrate with ZnO seeds was bathed in aqueous solution at different temperature conditions of 80°C, 90°C, 100°C, 110°C, and 120°C for 24 hours.

3. Double-Layered ZnO Nanostructures

Double-layered ZnO nanostructures were grown from ZnO nano rods in 0.1 M solution at 100°C for 24 hours. The Si substrate with ZnO nano rods was put into a dilute solution of 0.01 M at different temperatures of 80°C, 100°C, 120°C, 140°C, and 160°C for 4 hours, as shown in Figure 1.

III. Results and Discussion

The typical molecular structure of ZnO is known to be Wurtzite. The O^{2-} ions are located as hexagonal structures and the Zn^{2+} ion is located as a tetrahedron structures. ZnO is characterized by partial ion bonds, in which the presence of Zn^{2+} ions gives electrons to the O^{2-} ion. The (002) plane is relatively positively charged due to Zn^{2+} ion contributions. On the other hand, the (010) plane is rich in O^{2-} ions and so relatively negatively charged. Because of these ion bonding properties, compared to the O^{2-} layer, the Zn^{2+} layer has a relatively higher surface energy and faster growth rate.

Figure 2(a), (b). shows an XRD pattern and SEM image of the ZnO seed layers obtained using spin coating and curing processes, respectively. The SEM image confirms that the average ZnO seed diameter on the Si substrate is ~16 nm.

Figure 2. (a) SEM image of ZnO seed and (b) XRD spectrum.

To develop the ZnO nano rods, the ZnO seeds on the substrate are placed downward in a chemical solution bath with zinc-nitrate hydrate (0.1M) and hexamethylenetetramine (HMT) (0.1M) at different temperatures (80~120°C) for 24 hours. The chemical reaction formulae of the growth process is listed below as Eq. (1).

HMT is decomposed into formaldehyde (HCHO) and ammonia (NH_3), as expressed in Eq. (1). Ammonia (NH_3) reacts with water (H_2O) and dissolves to NH_4^+ and OH^- . The OH^- ions serve as a pH buffer, and the pH is between 6 and 7. In addition, the Zn^{2+} and OH^- ions from zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$) react with the zinc hydroxide ($Zn(OH)_2$). The zinc hydroxide ($Zn(OH)_2$) reacts to synthesize pre-fabricated ZnO seeds. Then, ZnO nano rods are grown from the ZnO seeds.

Figure 3(a) shows the XRD patterns of the ZnO nano rods at different temperature growth conditions. As the temperature of the chemical solutions rose from 80°C to 100°C, the (002) plane peak intensity increased slightly. And, at temperatures higher than 100°C, the peak intensity of the (002) plane tended to decrease; this is thought to be due to instability of the ion activation energy, which reduced the growth rate of the (002) plane. As a result, the specific area of ZnO decreased. XRD measurements show good agreement with our hypothesis.

The texture coefficient (TC) is extracted from the XRD data to confirm the orientation of the nanostructures. The orientation of the lattice can be calculated from each growth direction of the nanostructures by using TC. The direction perpendicular to the Si substrate is associated with the (002) plane. The formula for calculation of TC for the (002) plane is shown in Eq. (2). In this equation, I is the diffraction intensity measured by XRD and I^0 is the corresponding value from the reference data base (JCPDS

Figure 3. (a) XRD pattern of ZnO nano rods at different temperatures. (b) Texture coefficient and specific area of ZnO nano rods.

Figure 4. SEM images of ZnO nanorods at different temperatures of 80°C (a), 90°C (b), 100°C (c), 110°C, (d) and 120°C (e).

No.36-1451).

$$C_{002} = \frac{I_{002}/I_{002}^0}{\frac{I_{100}}{I_{100}^0} + \frac{I_{002}}{I_{002}^0} + \frac{I_{101}}{I_{101}^0} + \frac{I_{102}}{I_{102}^0}} \quad (2)$$

For example, if the value of TC_{002} is 1, all other aspects except plane (002) have not grown. Thus, the closer the value of TC_{002} is to 1, the closer the orientation of the nanostructure is to perpendicular to the substrate. Based on the reference data (JCPDS No.36-1451), $TC_{(002)}$ is 0.30 at 80°C, 0.56 at 90°C, 0.89 at 100°C, 0.78 at 110°C, and 0.84 at 120°C. We found that the nanorods for the best orientation of the (002) plane can be grown under the 100°C temperature condition. (Figure 2(b).)

The SEM images provided in Figure 4 confirm that the most common orientation of the ZnO nano rods is in the (002) plane. The average diameter of the nano rods is about 556 nm at 80°C, 528 nm at 90°C, 440 nm at 100°C, 241 nm at 110°C, and 130 nm at 120°C. The temperature condition and the average diameter show an inversely proportional relation. Also, the average heights of the ZnO nano rods are 1.19 µm at 80°C, 1.00 µm at 90°C, 1.15 µm at 100°C,

Figure 5. (a) XRD pattern of double layered ZnO nano structures grown at different temperatures. (b) Texture coefficient and specific area of double layered ZnO nano structures.

Figure 6. SEM images (a) ZnO nano rods synthesized in 0.01 M solution at 100°C and ZnO nano structures at different temperatures of (b) 80°C, (c) 100°C, (d) 120°C, (e) 140°C, and (f) 160°C.

1.01 µm at 110°C, and 1.23 µm at 120°C. To calculate the specific area of the ZnO nano rods, a six-sided area was added to the top area in the unit volume. Figure 3(b) shows the specific area of the ZnO nano rods for each growth condition.

Next, double layered ZnO nano structures were synthesized from ZnO nano rods under 100°C growth conditions; these were put into dilute 0.01M solution at different temperatures (80~160°C) for 4 hours. Figure 5. shows the XRD patterns of the double layered ZnO nano structures. The values of TC were 0.80 at 80°C, 0.79 at 100°C, 0.75 at 120°C, 0.75 at 140°C, and 0.91 at 160°C. The TC values show a decreasing tendency when the diluted chemical solution temperatures increased. Also, Figure 6. provides SEM images of the double layered ZnO nano structures. The first layer of ZnO nano rods covered the surface of the ZnO thin film. A sudden TC increment of the entangled porous thin membranes was observed in case of the 160°C temperature condition. As a result, the specific surface area rapidly increased.

When the concentration was reduced from 0.1 M to 0.01 M, the concentration of the Zn^{2+} ions in solution dropped and the growth rate decreased. The effects on the (002) surface with unstable surface energy were reduced, and the growth of sheet-like nanostructures in the (010) plane covered the ZnO nano rods.

Figure 6(a) shows the results of using an experimental method similar to that used in Figure 4, except that a dilute 0.01M solution was used at 100°C for 24 hours. Compared to the results shown in Figure. 4(c), the dilute (0.01M) solution growth results show a reduced orientation and unstable nano rods, as can be seen in Figure 6(f). Figure 6(b)~(e) show sheet-like ZnO membranes for a variety of temperature conditions of 80°C, 100°C, 120°C, 140°C, and 160°C, respectively.

IV. Summary

In conclusion, using chemical bath deposition and control of concentration and temperature conditions, we have demonstrated optimal growth conditions for sheet-like ZnO nanostructures on ZnO nano rods. The highest filling factor of sheet-like ZnO membranes was obtained for the 160°C growth temperature. Compared to simple

thin film nano rods, the specific area of the sheet-like ZnO membrane increased. We believe that our results of high specific area of sheet-like ZnO membrane provide a way toward the development of highly efficient sensing devices and their application.

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